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12th - 18th AUGUST 1950

CENTRAL LABORATORIES FOR SCIENTIFIC & INDUSTRIAL RESEARCH
HYDERABAD - DECCAN

PROCEEDINGS OF THE SYMPOSIA

ON

FUELS,

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With an inaugural address by

SIR J. C. GHOSH, KT., D. SC., F. N. I.,

DIRECTOR, EASTERN HIGHER TECHNICAL INSTITUTE,

CALCUTTA.

Edited by

DR. S. HUSAIN ZAHEER

DR. M. G. KRISHNA

Dr. M. S. IYENGAR (Fuels Section)

Dr. K. T. ACHAYA (Fats & Oils Section)

Mr. A. RAHMAN (Research & Industry Section)

FOREWORD

A symposium on Fuels, Fats & Oils, and Research & Industry was organised by the Central Laboratories for Scientific & Industrial Research, Hyderabad-Deccan, from 12th-18th August 1950. At the request of those who wished to attend and could not, and of those who attended, we decided to print the proceedings hoping that this volume might be of some use to others working in the fields covered by the Symposium.

The papers presented at the Symposium represented the trends of research in our country in their respective fields. They were of both fundamental and applied nature. One feature of the papers, as well as of the discussions that followed, was that they all tended to relate research and research problems with our national needs and demands We have given the latter prime importance and attention ; this was naturally one of our main purposes from the very start.

In the organisation of the Symposium we are indebted to the authorities of Osmania University for their very kind co-operation, especially to the Vice-Chancellor for his interest, and to Mr. P.V.R. Sebastian, Warden of the Osmania University Hostels, for arranging for the comforts of the delegates. We wish to thank Prof. S. Bhagavantham for the use of the Physics Lecture theatre for the inaugural meeting. We also owe thanks to the Secretary, Commerce & Industries Department, Government of Hyderabad, and to the respective managements, for having given us facilities to visit, on the 18th August, several factories.

The proceedings were recorded by members of the Central Laboratories for Scientific & Industrial Research who were participating in the Symposium, and we owe thanks especially to Mr. G. Satyanarayana Rao, Mr. R. Vaidyeswaran and Mr. Bharat Bhushan for their trouble in this respect.

Editorial Board

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NOTE

from

SIR J. C. GHOSH, Kt., D. Sc., F. N. I.

Director, Eastern Higher Technical Institute, Calcutta

" I am sorry that I cannot participate in the Symposium and that I am having to cause inconvenience to you at this stage due to my ill health. I wish your Symposia all success."

INAUGURAL ADDRESS*

by

SIR J. C. GHOSH

Director, Eastern Higher Technical Institute, Calcutta

I thank you for your kind invitation to inaugurate a symposium on fuels, vegetable oils and industrial relations which has been organised under the auspices of the Central Laboratories for Scientific and Industrial Research. I am glad to note that scientific workers from neighbouring States are participating in this symposium ; and I offer them on your behalf our most sincere welcome

The importance of utilising properly the resources in coal and vegetable oils of the State cannot be overemphasised. Much of the future industrial prosperity of the State will depend on the planned development of these resources.

Of these resources, coal is not renewable, and its utilisation is, therefore, linked up with the problem of conservation. Only scientific research can yield the knowledge on which a rational plan for utilisation and conservation of coal in Hyderabad can be based. Such work has already been started; and results of considerable interest have been published in the Records and Reports of the State Geological Survey and of the Central Research Laboratories. In this symposium two papers on the low-temperature carbonisation and fluidisation of Hyderabad coals will be presented for discussion.

You are probably aware that the Fuel Research Committee of the Government of India has been for sometime interested in the washability of Indian coals with a view to bringing down the ash content. Promising results have been obtained in the case of many coals in the neighbouring State of Madhya Pradesh. For example, coals from Chirimiri No. G. 65, from Newton Chikli No. G. 67 and from Kurasia No. G. 157 have given very statisfactory washability curves. The coals of the Hyderabad State owe their origin to similar geological conditions, and it is probable that some of the seams may give promise of

* Not delivered due to ill-health

economic cleaning. I therefore suggest that the Central Laboratories collaborate with the Fuel Research Committee of the Government of India in carrying out tests on the washability of Hyderabad coals.

South India has large deposits of high-grade iron ore but practically no deposits of coal which would yield metallurgical coke when treated according to conventional processes Hyderabad coals are mostly non-caking or weakly-caking The possibility of blending these coals with a certain percentage of coking coals from Jharia for making metallurgical coke should receive immediate attention. A good deal of information on this subject has already been incorporated in the Central Government's report on Blending of Coals for Coking, published in 1948. This report does not include any information on the blending properties of Hyderabad coal, and it is desirable that this gap in our knowledge should be filled in as soon as possible

You are no doubt aware that the Government of India has been considering for sometime the possibility of synthesising liquid fuels from Indian coals. The non-caking coals of Raniganj measures yield a low temperature tar which is suitable for economic hydrogenation. Contrary to prevailing ideas, it has been found, on semi-large scale trials, that samples of coal from Kajora, Disherghar and Lower Jamdoba seams give an yield of low-temperature tar amounting to 11 2 per cent and above Such high yields of tar naturally make these coals a very promising raw material for synthesis of petrol The Hyderabad coals are in many respects similar to coals of Raniganj measures I am, therefore, surprised that low-temperature carbonisation of Hyderabad coals has given yields of tar which do not generally exceed 9 3 per cent of the weight of dry coal and are for some samples as low as 5 26 per cent I suggest that this subject should be reinvestigated with greater thoroughness in the laboratory and such laboratory experiments confirmed by pilot-plant trials.

Among the renewable industrial resources of Hyderabad, vegetable oils occupy an important position, and in fact castor oil holds a key position. This oil is mostly used as such in industry or blended with other ingredients to produce valuable lubricants. A month ago, I happened to be in the United Kingdom; and there I was told of the inauguration of a new industry for the large scale manufacture of sebacic acid and capryl alcohol using castor oil as raw material. You are no

doubt aware that the cracking of castor oil leads to a variety of interesting products, of which one reaction is noted below .—

$$CH_3(CH_2)_5CHOH.CH_3 + HOOC.(CH_2)_8COOH + H_2$$

2 Octanol — Sebacic acid.

These laboratory results have now been transferred to large scale industrial practice. The Geigy Company of Manchester has joined hands with the Hardesty Chemical Company of New York and have just completed the construction of a large plant at Trafford Park, Manchester, which will meet the rapidly-increasing demand for these two products by the plastics industry of Western Europe. The uses of sebacic acid are rapidly increasing. It imparts to its derivatives a much higher degree of plasticising efficiency than the dibasic acids, such as phthalic acid, which are now commonly used. In the production of polyesters, of which the alkyds are typical examples, and in the production of polyamides of the nylon family, sebacic acid has already proved its potentialities. The substitution of phthalic and adipic acids by sebacic acid is rapidly growing in industrial practice; and hence sebacic acid has the assurance of an ever-expanding market. The octyl alcohol obtained from castor oil is the parent material for octyl-ester plasticisers and is also a solvent for urea-formaldehyde and polyvinyl-acetal resins. It can also be used as a substitute for butanol in many operations.

This State is the largest centre for the production of castor oil in the Commonwealth; and I hope that some day in the near future, as a result of the work of the investigators here, this State will also be the most important centre in the Commonwealth for the industrial processing of castor oil; and that we shall not export castor oil as such, but only the finished chemicals derived from this oil. I wish the workers of the Central Laboratories all success in this enterprise.

OPENING SESSION

SATURDAY, 12th AUGUST, 1950

Introductory Remarks

Dr. S H. Zaheer, Director, Central Laboratories, Hyderabad-Deccan, opening the Symposium, expressed his regrets at the unavoidable absence of Sir J. C. Ghosh who was to have inaugurated the symposium Unfortunately, since his return from England, Sir Jnan had been ill with influenza and was unable to be present, however he hoped that the address would be received and read in the course of the symposium

Continuing, Dr. Zaheer explained as to why the symposium had been arranged He hoped that this would be the beginning for a series of such symposia to be arranged by various institutions in coming years. There was a great need in India for discussion pertaining to the various problems being tackled in different research institutes, an exchange of experiences of various research workers through personal contact was highly desirable

Dwelling on the possibility of duplication of research work at various institutes, the speaker said that though in India unnecessary duplication should no doubt be avoided, it would nevertheless be a great advantage if a problem were to be tackled at different places from different angles. Some amount of duplication was unavoidable, and it was therefore all the more necessary to bring together workers investigating the same problem, so that the different approaches could be compared and discussed.

The speaker then went on to explain why the three topics featured had been chosen for the symposium. Hyderabad has as its main raw materials vegetable oils and coals, and the Central Laboratories, being mainly concerned with the development of local resources, has been concentrating on problems concerning their utilisation. Hence it was considered very desirable to include these two subjects. Broad fields in these subjects had purposely been selected so as to attract a sufficiently representative gathering to this first symposium. Moreover there was a dearth in India of highly specialised workers in these fields On the basis of the present experience, specialised subjects might well be chosen for future symposia.

Further, the speaker continued, there was great need for co-ordination of work being done in various laboratories all over the country in order fully to develop national industries. The lack of proper development of industries so far necessitates a scientific study of the causes for this, and Operational Research would provide the necessary method. Operational Research had been a potent factor in winning the last war; its importance in times of peace has now been realised and it is being successfully utilised to this end in the U K , U S.A and U.S S R. In order to help the research worker, a detailed study of his problem from a socio-scientific point of view is undertaken in the Central Laboratories by a small Operational Research Unit; this Unit also co-ordinates the advancement of research from the laboratory to the pilot plant level, and thence to the industrial plane, and will also follow the efficiency of working in the last phase

Finally Dr. Zaheer remarked that the functions and scope of this Symposium on fuels, fats and oils, and research and industry did not conflict with the much wider work of the Indian Science Congress Association ; on the other hand, he emphasised that such symposia were meant to supplement the former He again expressed the hope that the organising of such symposia would be taken up by other institutions, and appealed to his audience to co-operate in inducing other scientists to participate in any future venture of this kind. In conclusion, he wished to take this opportunity to express his thanks to his colleague, Mr. A Rahman, Operational Research and Intelligence Officer, Central Laboratories, with whom this idea of holding a symposium had originated, and who had been responsible for its organisation.

Additional Remarks

After Dr. Zaheer's introductory remarks, the guests were requested to give their opinions on the various points he had made.

Dr. H. G. Kayser, speaking first, welcomed the decision of Dr. Zaheer and the Central Laboratories to hold a symposium of this kind and thanked them for having invited him to take part. He said that such gatherings were very necessary so that scientists and technologists from all over India could come into personal contact and exchange views. He thought that the selection of subjects had been most appropriate, and that at the present stage of science in the country discussions should be conducted on general topics rather than on highly specialised

subjects. Referring to duplication of work, he agreed with Dr. Zaheer that unnecessary duplication should be avoided in tackling problems, though it had often happened that duplication had helped to advance a subject. In conclusion Dr Kayser hoped that such symposia would be held frequently by others also and wished the present venture all success.

Dr M. R. Mandlekar thanked the organisers for the invitation extended to the Department of Industries, Government of Bombay and commended the idea of holding this symposium He said that there was great need for industrial research in the country today; industrial development was at a low level in spite of the industrialists and the Government doing their best It was necessary, he added, for Government laboratories after thay had worked out a problem, to actually help industrialists to establish the process commercially on a sound basis In order to bring about the maximum co-ordination of research work being done all over the country and in order to have a free exchange of knowledge such symposia were a necessity. He wished the symposium every success.

Dr J S Aggarwal congratulated the authorities of the Central Laboratories for having taken the initiative in starting a symposium of this type, he had little to add to what the others had said. In his brief visit round the Laboratories he had been much impressed with the work and spirit of the place

Prof B N. Banerjee commended the symposium for focussing attention on the vegetable oils of which there was great shortage in India Dealing at some length with the national needs and food problems of the country, Prof Banerjee said that the daily consumption of fats in India was appallingly low today Oils were liable to go rancid resulting in much waste of food material and this could and should be prevented

MESSAGES

Dr. N. N. Dastur,
Indian Dairy Research Institute,
Bangalore

"I send my best wishes for the success of the Symposium which covers subjects of such great importance to our country"

Dr. S. P. Pathak,
Assistant Professor,
Department of Industrial Chemistry,
Banaras Hindu University.

"I congratulate you for having conceived this brilliant idea of arranging a Symposium on various burning topics of the day along with the fundamental researches in those lines. This would really be a nice opportunity for us all to get personal and direct contact with the subject and people of the line"

Dr. J. G. Kane,
Department of Chemical Technology,
Bombay.

"You have been able to get a very substantial and interesting programme for the forthcoming Symposium indeed, and I congratulate you heartily . I wish I were able to attend. But this being the midst of our regular term I am unable to leave Bombay"

Dr. D. R. Dhingra,
Principal,
Harcourt Butler Technical Institute,
Kanpur.

"I will try to come there and take part in the Symposium which will be very interesting and instructive."

Mr. W. M. Vaidya,
National Physical Laboratory,
Delhi.

"Many thanks for your kind invitation to attend the Conference. I would have been very glad to attend but as things are I find it very difficult to leave Delhi I wish your conference every success."

SYMPOSIUM ON FUELS

Edited by

Dr. M. S. IYENGAR

President: Dr. Ing. H. G KAYSER, Director,
Laxminarayana Institute of Technology,
Nagpur.

BRIQUETTING AND LOW TEMPERATURE CARBONISATION OF NON-CAKING INDIAN COAL

by

DR M S. IYENGAR

Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn.

A self-supporting process for briquetting non-caking Bellampalli coal, based on the Hodsman process, is described. The Hodsman process essentially comprises increasing the viscosities of low temperature tars by treatment with lime. The briquettes obtained are subjected to low temperature carbonisation. The tar recovered is used to briquette further lots of fresh coal, and the carbonised briquettes are used in the smelting of iron ores by the Tysland-Hole Electric furnace.

Introduction

The present annual production of coal of size 0-1/8 of an inch in India can safely be estimated as roughly 40 percent of the total saleable coal produced, in other words, for every 10 million tons of coal produced annually, an extra 16 million tons of coal in the form of fines are produced. Most of these fines at present find little or no use and are therefore wasted It is well understood that the development of mechanisation in mining generally increases the production of fines which are difficult to utilise by reason of high ash and moisture content. Since mining is likely to become more mechanised in India and coal cleaning a general practice still greater quantities of fines will be produced. In the conservation of our coals suitable use will have to be found for the coal fines The present paper deals with a process developed for the upgrading of fines, based on briquetting and low temperature carbonisation.

Most briquetting processes rely on apparent cohesion where wetted particles of coal are pressed closely enough for capillary forces to operate Here the wettability of coals are critical and depend upon their rank. In general the lower rank coals are more easily wetted by water and those of higher ranks by pitch or tar. It is for this reason that lower

rank coals can be briquetted merely by application of pressure, whereas to briquette higher rank coals, a binder like pitch or tar is needed in addition to pressure.

Nearly all the non-caking Indian coals are of medium rank in age, and hence can be briquetted only on addition of a suitable binder. The normal binder used in other countries is pitch. But this has a number of shortcomings . (*a*) low fusion temperature and consequent disintegration of the briquette on combustion, (*b*) smoke production, (*c*) difficulty in handling, and (*d*) limited supply and high cost. These reasons added to a very limited supply of pitch available in India makes its use in briquetting unsuitable Various vegetable and inorganic substitutes have been tried for pitch but with limited success

The briquetting process described in the present paper utilises the Hodsman process in the production of suitable binder The Hodsman process consists essentially in increasing the viscosities of certain types of tars by allowing them to react with lime at elevated temperature, when the tar acids react with lime and cause abnormal increase in viscosities. This reaction can be carried out on the surface of aggregate particles of coal even at room temperature.

Materials

All the experiments described in the present paper were carried out on Bellampalli coals The proximate and ultimate analysis of this coal is given in Table I

TABLE I.

ANALYSIS OF BELLAMPALLI COAL

Proximate analysis %		Ultimate analysis %	
		Substance	Air-dry basis
Moisture ..	6 87	Carbon	69 20
		Hydrogen .	4 93
		Oxygen	8 80
Volatile matter	29 59	Nitrogen	1 50
Fixed Carbon .	49 47	Sulphur	1.50
Ash ..	14 07	Ash .	. 14 07

The Lime-Tar Reaction

Normal tars behave as Newtonian fluids, their viscosities being independent of the rate of shear. However, by treating a vertical retort tar with lime and water at elevated temperatures, combination of the acidic constituent with lime takes place resulting in an enormous increase in viscosity. The products no longer behave as Newtonian fluids, yet acquire a pronounced rigidity requiring the application of an appreciable force to cause movement. This is attributed to the formation of a structural frame-work within the body of tar which increases in strength on standing without disturbance.

Not all tars are equally susceptible to lime-treatment. Tars essentially of paraffinoid or non-aromatic character, like vertical retort tar or low temperature tar, respond most readily. In Figure 1 (*see page* 16) is shown the increase in viscosity of different types of tars on treatment with lime. It will be noticed that coke-oven tars and high temperature tars hardly show any increase in viscosity, while low temperature tar is very reactive.

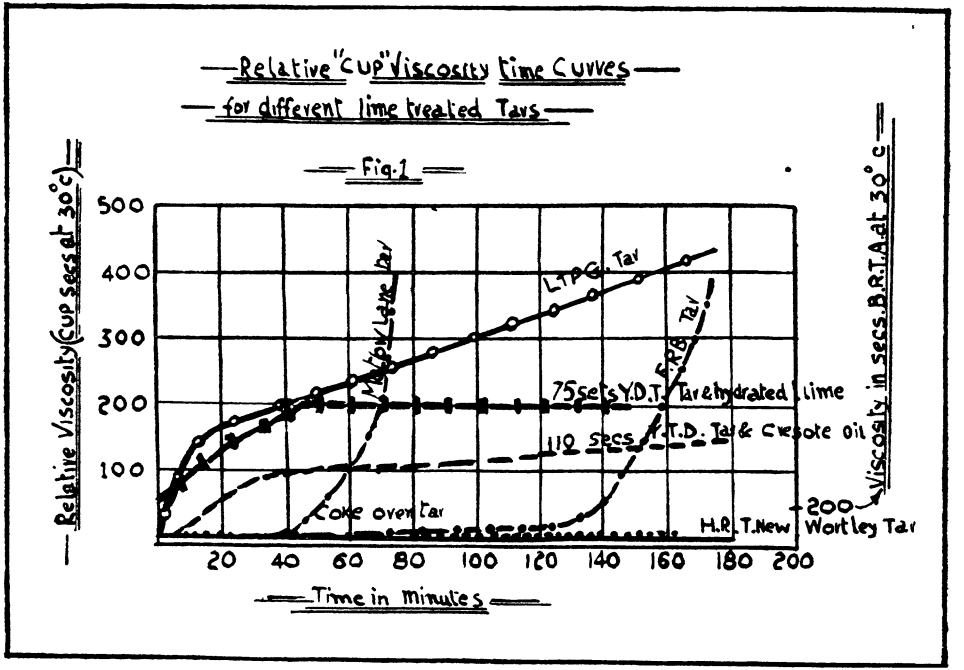
One of the remarkable properties of the lime-tar reaction is the setting to 'cheese' of the products of reaction on allowing them to stand undisturbed. This 'cheese' is less susceptible to temperature fluctuations than pitch or other similar material (*see* Figure 2, *page* 17).

The Bellampalli tar used in these experiments was obtained by distilling Bellampalli coal in a thermic carbonisation plant. The temperature in the retort was maintained between 600-650 C. at the time of charging. The properties of the tar are shown in Table II.

TABLE II.

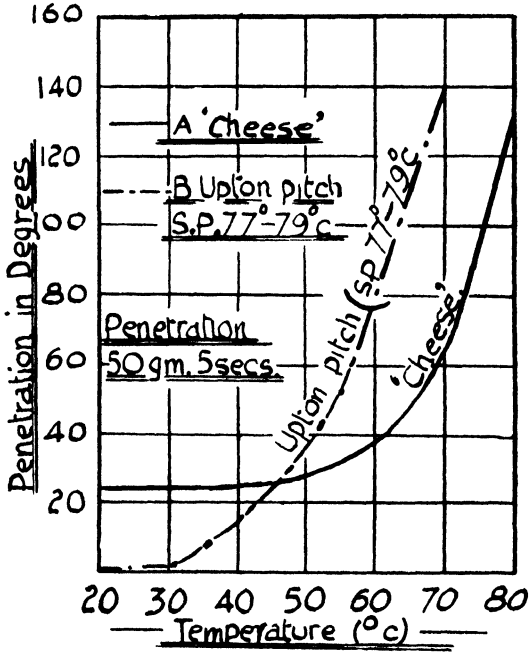
Analysis of Low temperature Bellampalli tar

	as sampled	Calculated on water free basis
Sp. Gr. at 15 5°C.	1.114	1 143
Water (Dean & Stark)	12 0%	.
Tar acids	16 5%	18 7%
Total oils	50.0%	56 8%
Oils to 170°C	6 0%	6 8%
170 – 230°C.	25 0%	28 4%
230 – 300°C.	19 0%	21 5%
Viscosity of crude tar (Cup method)		8--10 secs. B R.T.A. at 30°C.
Viscosity on dehydration (Cup method)		300-350 secs. B.R.T.A. at 30°C.

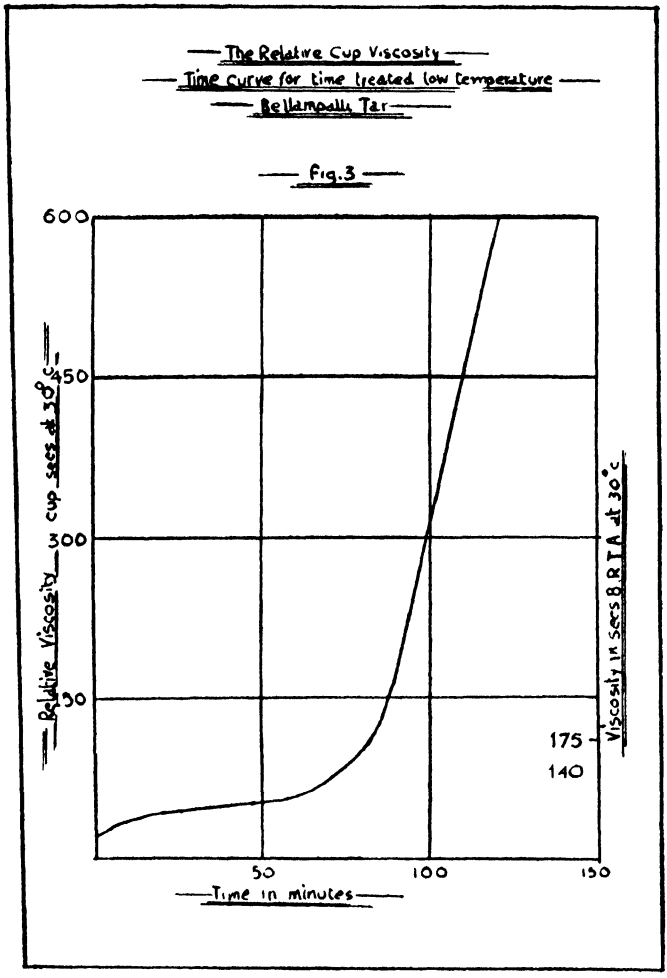

Relative "Cup" Viscosity time Curves
for different lime treated Tars
Fig.1
Relative Viscosity (Cup Secs at 30°C)
Viscosity in secs. B.R.T.A. at 30°C
500
400
300
200
100
20
40
60
80
100
120
140
160
180
200
Time in minutes
L.T.P.C. Tar
Maltby Lathe Tar
F.R.B. Tar
75 secs Y.D.T. Tar & hydrated lime
110 Secs T.D. Tar & Creosote oil
Coke oven Tar
H.R.T. New
200
Wortley Tar

Influence of Temperature on the Penetration of 'Cheese' & Upton Pitch.

Fig. 2



On allowing the Bellampalli tar to react with lime at 70°C. the viscosity of the tar increased from 10 secs B.R.T.A. to over 600 secs. B.R.T.A. at 30°C. in two hours (*see* Figure 3 *below*.)



Laboratory scale experiments on the application of lime-tar reaction to briquetting of Bellampalli fines.

The experimental procedure adopted was that coal was first crushed to below 1/8 inch in a jaw crusher and then in a roller press. A typical sieve analysis of the fines used is shown in Table III.

TABLE III

SIEVE ANALYSIS OF BELLAMPALLI FINES

Over 1/6-inch	14 2%
1/6-1/8-inch .	. 21.8%
1/8-1/20-inch ..	.. 56 7%
Under 1/20-inch	. 7.3%

About 400 grams of the crushed coal were taken and to it were added about 2-10 grams of lime and 40-60 grams of tar. As the coal and tar both contained sufficient moisture no additional water was used The mixing was done in an ' Hobart Mixer.' Briquettes were obtained by pressing suitable quantities of the mix in a laboratory hand operated hydraulic press using cylindrical moulds The pressure used was about 2000 lbs./sq in. The briquettes thus obtained continued to set by chemical reaction. The strength of the briquettes were determined periodically by taking their crushing load in a ' Slaters ' Compression testing machine The briquettes were regularly carbonised in a gas fired laboratory furnace maintained at 600°C and the carbonised briquettes were tested for their strength.

The results of laboratory scale experiments can briefly be summarized as follows :

1. The lime-tar reaction provides a suitable binder for briquetting.
2. It is advantageous to carry the lime-tar reaction within the body structure of the briquettes rather than to allow it to proceed externally and then introduce it into the mix.
3. Bellampalli tar is more reactive to lime treatment than high temperature tars. However, this tar seems to have one disadvantage, *viz*, the briquettes prepared with this tar increase in their strength on storage only upto a point and then gradually weaken This phenomena is more pronounced in the case of briquettes prepared with quick-lime than with slaked-lime.

4. Best results were obtained with briquettes having the following composition :

Coal	..	400 grams
Tar ..	..	60 grams
Slaked-lime	..	4 5 grams

5. The carbonisation of the briquettes at 600°C. indicated that not all tar is recovered from the briquettes. This might probably be due to the tar acids in the tar reacting with lime and getting 'fixed.' The percentage of tar that gets fixed depends on the period of storage prior to carbonisation and on the mode of carbonisation. The best results were obtained when briquettes were allowed to stand over-night at room temperature and then carbonised at 600°C. for one hour. The tar recovered is also reactive to lime treatment and can be used to briquette a fresh lot of fines.

Semi-Industrial scale Experiments

The experiments carried out on a laboratory scale did not give sufficient information about the products obtained by carbonisation of the briquettes. The quantities used were too small and the yields from carbonisation were of the order of a few grams with the result that it was not possible to study fully the properties of the carbonised briquettes and the recovered tar ; nor was it possible to establish clearly whether the process could be made self-supporting.

Experiments were carried out on a semi-industrial scale and these experiments are represented schematically in Table IV (*see page* 22).

About 30 lbs. of coal crushed to 2-inch were carbonised in a horizontal gas-fired thermic plant at 600 -650°C. for about 2½ hours. The tar obtained was mixed with Bellampalli fines and slaked-lime in suitable proportions and briquetted in a hammer mould. The briquettes were allowed to stand over-night and then carbonised at 600-650°C. for 2½ hours in the thermic plant. The residue was dry quenched. The tar recovered was reused to briquette fresh lots of fines under similar conditions and the process was repeated to three generations. After each carbonisation, the carbonised briquettes and the tar were examined. The layout of the 'thermic' carbonisation plant used in these experiments is shown in Figure 4 (*see page* 21).

Fig. 4

DIAGRMMATIC PICTURE OF THE EXPERIMENTAL PLANT.

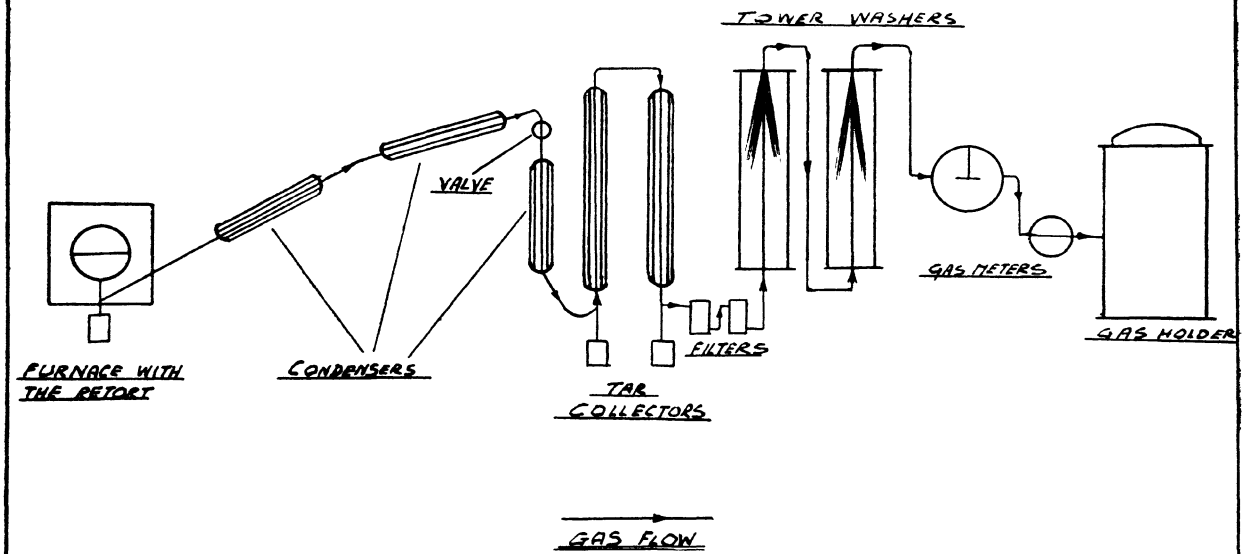
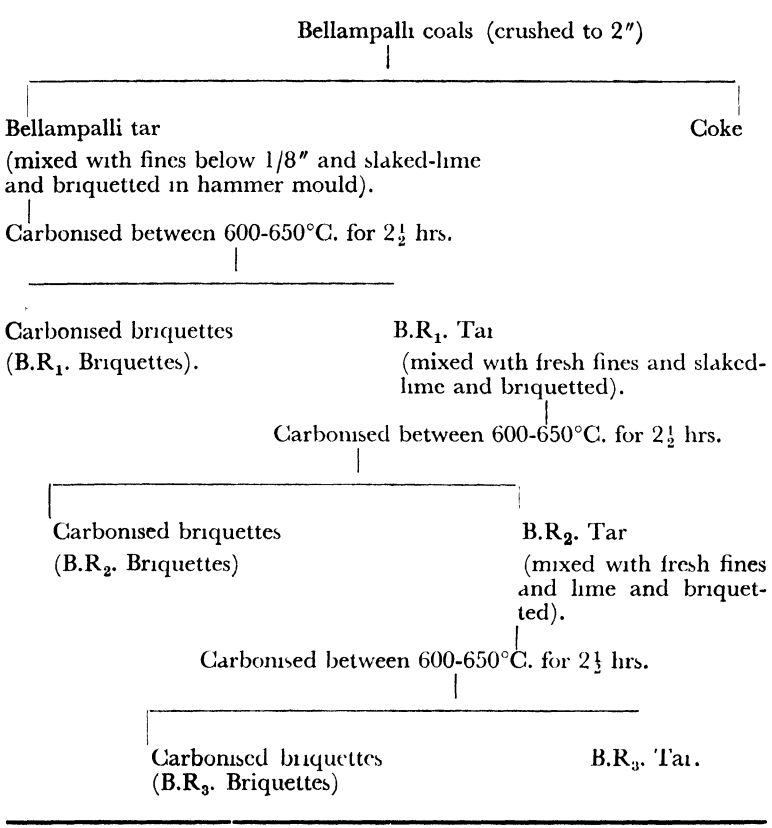


TABLE IV

SCHEMATIC REPRESENTATION OF THE CONTINUOUS PROCESS FOR BRIQUETTING AND CARBONISING BELLAMPALLI COALS



A typical sieve analysis of the fines and the composition of the mix used in these briquetting experiments is shown in Table V (*see page* 24).

The properties of different generation tars are shown in Table VI. It will be seen that the tar acid content slightly falls after each distillation ; also the viscosity of the tar decreases. The original tar which contained about 12 per cent. water and had a viscosity of 8 secs. B.R T.A at 30°C. showed remarkable viscosity changes on dehydration, increasing from 8 secs. B.R.T.A. to 300 secs. B.R.T.A. at 30°C. However,

the recovered tar did not exhibit this phenomena. Also, as is evident from Figure 5 (*below*), the reactivity of the tar to lime treatment decreases with each distillation.

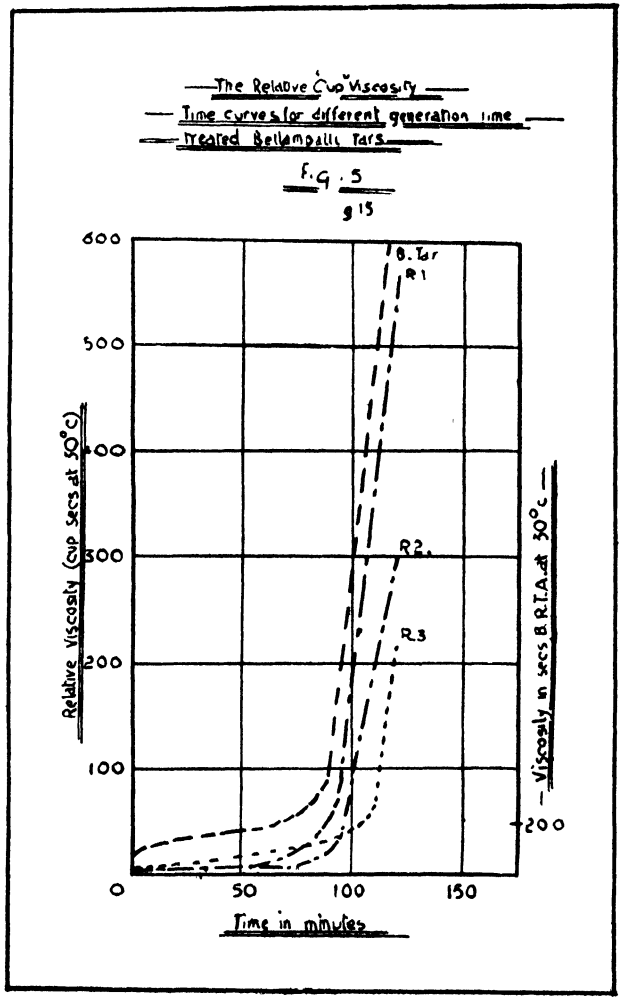


TABLE V

SIEVE ANALYSIS AND COMPOSITION OF THE MIX USED FOR BRIQUETTING EXPERIMENTS

Sieve Analysis of fines :	
Over 1/6 inch ..	3.2%
1/6-1/8 inch . ..	7.8%
1/8-1/20 inch	62 1%
Under 1/20 inch ..	26 1%
Composition of mix :	
Bellampalli fines	.. 20,000 grams
Tar ..	.. 3,000 grams
Slaked-lime ..	. 218 grams

The physical properties and reactivity of the carbonised briquettes obtained after each distillation are indicated in Table VII. From the Table it will be seen that the moisture, ash and volatile matter content increases after each carbonisation Also, what is more important and advantageous, the reactivity of the carbonised briquettes increases after each distillation.

Utilisation of the Carbonised Briquettes

One of the main important uses to which the carbonised briquettes obtained in the above process can be put is in the smelting of iron ores in the Tysland-Hole electric furnace Samples of the carbonised briquettes were sent to Messrs. Elektrokemisk, Oslo (a firm which has specialised in the installation of Tysland-Hole electric furnace) and the results of the tests they carried out are presented in Table VIII. On the basis of these results the firm concluded that the briquettes can be used as reductants in the smelting of iron ores in Electric smelting processes.

TABLE VI

THE PROPERTIES OF DIFFERENT GENERATION TARS

(dry basis)

	B. Tar	$B.R_1$.Tar	$B.R_2$.Tar	$B.R_3$ Tar
Sp gr. at 15 5°C	1 143	1 0780	1 0840	1 0900
Tar acids (% of tar)	18 74	16 66	14 19	13 69
Oils to 300°C. (% tar)	57 00	55.00	51 00	45 00
Distillation ·				
Oils to 120°C.	0	7.0	4 0	3.0
120 – 170°C.	7 0	1 0	1 0	2 0
170 – 230°C.	28 0	26 0	25 0	18 0
230 – 300°C.	22 0	21 0	21 0	22 0
Water content (% of wet tar)	12.0	10 0	8 4	12.0
Viscosity (at 30°C. Redwood No. 2 secs)	1252	93	34	40
B.R T.A .	8	1	–	–
Viscosity on dehydration Redwood No. 2 .	–	200	150	170
B R.T.A. ..	300	2	1	1

TABLE VII

THE PHYSICAL PROPERTIES OF DIFFERENT GENERATION CARBONISED BRIQUETTES

	B. Coke	$B.R_1$. Coke	$B.R_2$. Coke	$B.R_3$. Coke
Moisture (loss at 105°C.)	1 5%	1.9%	3.0%	4 0%
Ash ..	18.0%	19 0%	16.6%	19.6%
Volatile matter (less moisture) .. .	9.0%	12.5%	11.8%	11.4%
Fixed Carbon ..	71.5%	66.6%	67.6%	64.0%
C.A.B. (cu. ft. min.) ..	0.020	0 194	0.0202	0.186

TABLE VIII

REACTIVITY & ELECTRICAL RESISTANCE OF BELLAMPALLI COALS AND BRIQUETTES

	Reactivity	Resistance
Bellampalli coal	2,1	2700 ohm mm².m.
Coal briquetted with tar and slaked-lime and carbonised at 600°C.	2,5	2400 ohm mm² /m.
Coal briquetted with producer tar and slaked-lime and carbonised at 600°C	2,3	4100 ohm mm² /m.
Cinders	0,29	1050 ohm mm² /m.

Acknowledgement

The author takes this opportunity of thanking Mr. H. J Hodsman, The University, Leeds for his keen interest, valuable guidance and help throughout this work , his thanks are also due to the University of Leeds for allowing this paper to be published.

(*Saturday*, 12*th August* 1950)

DISCUSSION

Participants :

1. Dr. H. G. Kayser, Laxminarayana Institute of Technology, Nagpur. (Chairman)
2. Dr. S. Husain Zaheer, Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn
3. Mr. Sayed Kazim, Mines and Geological Survey, Hyderabad-Deccan.
4. Dr. K. Venkateshwar Rao, Mines & Geological Survey, Hyderabad-Dn.
5. Dr. M. R. Mandlekar, Commerce & Industries Department, Bombay.
6. Mr. G. Rama Rao, Osmania Technical College, Hyderabad-Deccan.

7. Dr. M. S. Iyengar, Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn.

8. Mr. S. S. Ghosh, Indian Institute of Science, Bangalore.

Several questions were asked regarding the *necessity of measuring viscosity* (H.G.K.), *advantage in using slaked-lime* (H.G.K.), *the criterion for fixing the proportion of slaked-lime to tar* (S.H.Z.) and *the basis for assuming chemical reaction between slaked-lime and tar* (K.V.R.).

In reply it was stated (M S.I.) that in briquetting processes two types of forces came into play One was the capillary force and the other was that due to chemical bond. The first type of force always came into play whenever coal was wetted by substances like pitch, tar, or water and briquetted In the experiments described slaked-lime reacted with the tar acid in the tar on the surface of the closely pressed particles of coal and combined the advantages of both the capillary forces as well as the chemical bond Since, in the process the reaction of slaked-lime with tar was the operative part in determining the strength of the briquettes, a knowledge of the reactivity of tar to slaked-lime was essential Viscosity measurement helped to assess the reactivity of tar to slaked-lime and was therefore used in these experiments The proportion of slaked-lime to tar was fixed by assuming that slaked-lime reacted with the tar acid, determining the tar acid content of the tar and calculating the corresponding amount of slaked-lime required to react chemically The basis for assuming chemical reaction was that when a lime-treated tar was distilled it was found that no tar acid was present in the distillate

It was pointed out (H G.K.) that *the gradual weakening of the briquettes on storage* might be due to the shrinkage in the structure of bound humic acid that was probably present in the briquette. Experience in Germany had indicated that the German brown coal contained humic acid in bound and in free form Bound humic acid (bound with alkali) had a colloidal structure which shrank on absorption of moisture from the atmosphere. By suitably controlling the quality and quantity of slaked-lime it might be possible to minimise the weakening of the briquettes.

Questions were asked (G.R R.) regarding *the composition of the material of thermic plant, mode of heating the furnace, percentage of volatile matter* in the carbonised briquettes and the comparatively *shorter duration of carbonisation.* In reply it was stated (M.S.I.) that the thermic plant was constructed of an alloy of mainly nickel, chromium and iron with traces of tungsten, manganese, and silicon ; the retort was gas heated

with six burners ; the carbonised briquettes contained 9-11 per cent. volatile matter. In the normal carbonisation practice the charge was heated from the cold and hence took a longer time for carbonisation, whereas in the experiments described the retort was already heated to 600°C. and then charged.

An opinion was expressed (G.R.R) that since according to data presented not all *tar used in briquetting is recovered* from carbonisation, the stock of tar for briquetting would have to be constantly replenished. It was however felt (M.S.I.) that after each distillation of the briquettes the tar that could potentially be recovered from the coal of the briquettes was not recovered, but the amount of tar used in briquetting was recovered. From the point of view of the tar needed for the briquetting of the next lot of fines, the process could be made self-supporting However in practice this could not be achieved as (as was evident from data presented) the reactivity of the tar decreased after each distillation so that after four or five operations the tar would have to be replenished with fresh tar.

Regarding *comparison of the process* with other existing blending processes for the manufacture of coke (S.H.Z.), it was felt (M.S.I.) that in the case of Singareni or Bellampalli coals, they would have to be blended with 9 times their amount of caking coals in order to obtain a suitable coke by any of the blending processes available, which therefore depended on the availability of large amounts of caking coals. As opposed to this the process presented was a self-supporting process for obtaining suitable coke from the coal

It was pointed out (K.V R) that since in the briquetting process slaked-lime was added, *the ash content* in the carbonised briquettes increased. It was however felt (M S I.) that the amount of slaked-lime used was a fraction of a percentage of the coal and would not increase the ash content markedly ; besides even the slight fractional increase in ash content was not disadvantageous as it actually increased the *reactivity* of the briquettes. The reactivity was determined (M.S.I.) by the available standard methods One method depended on the determination of the critical air blast above which combustion of fuel bed continued and below which combustion was extinguished The other method depended on the determination of the CO to CO_2 ratio when CO_2 was passed through a bed of fuel maintained at 900°C. An opinion was expressed (S S.G) that the high reactivity of coke was undesirable in blast furnace operations ; also that the briquettes obtained

in the process may not withstand conditions in blast furnaces. However it was felt (M.S.I.) that one had to be careful while discussing reactivity of coke. If the coke was to perform the functions of (*i*) providing the necessary heat for smelting, (*ii*) acting as a reductant and (*iii*) acting as a carborising agent, then high reactivity of coke was a disadvantage ; but in operations like electric smelting where the coke performed only the functions of a reducing and carborising agent, a high reactivity of coke was an advantage. The carbonised briquettes obtained were suitable for electric smelting only and not suitable for blast furnace operations.

Questions were asked (S K) regarding *the economics of operating the process* on an industrial scale, and the competent authority for undertaking the process. In reply it was stated (M.S.I) that the experiments presented pertained to work carried out on a semi-industrial scale only and these experiments did not establish conclusively the economics of the process. However it might be said that since the cost of fines and lime is very low, the process should be economically workable on an industrial scale. The competent authority to undertake the operation of the process would be the colliery management.

In reply to a question (M R M) on the feasibility of *underground gasification of coal* for Indian conditions, it was stated (H.G.K.) that the process was of recent origin and like any new process (like fluidization) wild claims were made of the many advantages of the process There were a number of difficulties which were to be overcome in underground gasification processes. The coals in seam were not evenly distributed with the result that only 65 per cent of coal would be recovered by the process Also before starting operations the seam had to be divided into rectangular blocks necessitating considerable amount of masonary work underground. There was always the possibility of frequent explosions and fires in the process. Before the process could be adapted to Indian conditions a lot of spade work would have to be done on the geological distribution of coal and sufficient data would have to be collected on the economic feasibility of the process for Indian conditions. The process was economically feasible for coals with as high an ash content as 75 per cent and over. Another point to be borne in mind was that the process made available large quantities of gas near the pit head whereas most of the Industries were situated away from the mines. This brought the problem of long distance transport. It might well take another 10 years before the process became suitable for Indian conditions (H.G.K.).

FLUIDIZATION OF HYDERABAD COALS

by

G. SATYANARAYANA RAO AND M. S. IYENGAR

ntral Laboratories for Scientific & Industrial Research, Hyderabad-Dn

General fluidization principles are reviewed briefly, and the ture of earlier data discussed. Flow characteristics for con- uous fluidization of Singareni coals in a glass column, 1 in. diameter and 4 ft. long, have been investigated. The aver- e solid concentration for different solid feed rates and air tes were determined. It is observed that the average solid ncentration is maximum at low air rates and decreases as the w of air is increased.

roduction

In recent years, fluidization has received considerable attention an improved method of achieving gas-solid contact in industrial ocesses, particularly for the catalytic cracking of petroleum At sent, it is being considered for a number of other chemical operations, h as synthesis of liquid hydrocarbons, production of phthalic anhy- de, and gasification of coals In our laboratory we are attempting nstal an experimental plant for carbonisation (and gasification) of derabad coals using the technique of fluidization In order to ign this unit, it is necessary to have a clear picture of the factors essary to obtain satisfactory operation of the fluidization unit. The a presented in this paper cover preliminary investigations carried on the continuous fluidization of Singareni coals.

view

Batch fluidization.—Papers by Wilhelm and Kwauk (2, 3), Max Leva l his co-workers (4, 5, 6, 7), Morse (8) and Matheson, Herbst and lt (9) provide the most satisfactory theory and criteria for batch dization presented to date.

Fluidization is characterized by counter gravity flow of fluids ough beds of fine solid particles. In an analysis of pressure drop- d velocity relations of such a system, it has been observed by a number

of workers (2, 3, 4, 5, 6, 7, 10, 11, 12) that the bed begins to expand at a definite fluid velocity. Although the pressure drop increases steadily with the fluid velocity for flow through an unexpanded bed it remains essentially constant for flow through expanded beds. Mathematically expressed :

$$\Delta p = \frac{V_T}{A_T} (1-\varepsilon) (\rho_s - \rho_f) \qquad \mathbf{1}$$

The validity of this expression was tested by many investigators (2, 3, 4, 5, 6, 7, 10, 12) and found to be independent of such system properties as material density, shape and size of particles, weight-size distribution of charge, fluid density, viscosity and geometry of the vessel. Particle size ranges supporting equation **I** extended from 600-mesh or finer (12) through fine-grained sands and iron Fischer-Tropsch catalysts (4, 5, 6, 7) upto particles 0 25 of an inch in diameter (2, 3). Various gases as well as water were used as fluids and the vessel diameter varied between 1 and 6 inches.

Experimental data observed by Max Leva and his co-workers indicate that before a bed of solid particles pass into fluidized state — *i e*, exhibit internal particle motion — a definite amount of bed expansion is required in order to disengage the particles sufficiently from each other. The fraction voids associated with this condition (' minimum fluid voidage ') was found characteristic of the shape and size of the particles. In general, small and irregular particles require a higher minimum fluid voidage than more regular and larger shapes.

For non-fluidized range, according to Carman (13) the pressure drop is related to other system variables by the equation .

$$\Delta p = \frac{2f\, G^2 L \lambda^{(3-n)} (1-\varepsilon)^{(3-n)}}{D_p\, g_c\, \rho_f\, \varepsilon^3} \qquad \mathbf{2}$$

Combining **1** and **2**, and substituting ε_{mf} for ε, and solving for the mass velocity yields .

$$G_{mf}^2 = \frac{D_p\, g_c\, \rho_f\, (\rho_s - \rho_f)\, \varepsilon_{mf}^3}{2f\, \lambda^{(3-n)} (1-\varepsilon_{mf})^{(2-n)}} \qquad \mathbf{3}$$

a general equation which can be used to predict the onset of fluidization.

Inasmuch as the pressure drop remains essentially constant for the fluidization range, it follows that, if equation **2** applies, a plot of log $\frac{G^n . \mu^{(2-n)}}{\rho_f} Re$ Vs log $\frac{(1-\varepsilon)^{(3-n)}}{\varepsilon^3}$ should yield a straight line of slope m=−1 for any type of bed. Use of this equation indicated that particles of comparatively large diameter obeyed the equation, whereas, with small materials, deviations were observed that became progressively more significant as the particle diameter decreased. Interpretation of the data led Leva and his co-workers to the concept of fluidization efficiency. Thus

$$\phi = \frac{G_F - G_c}{G_F} \qquad 4$$

Wilhelm and Kwauk (2, 3) studied the fluidization characteristics of various materials using water and air as the fluid, and noted an important difference between fluidization with water and fluidization with air. In the former case, the bed is made up of agitated, well dispersed particles, and the water rises between individual particles. In the later case, however, the particles are not well dispersed, but tend to agglomerate into clumps or aggregates, which tend to move to one side and allow the gas to pass as a ' bubble ' or else are carried upwards as slugs by the gas. The first case is termed particulate fluidization and the second, aggregative. The difference between the two cases is one of difference in the degree of segregation Morse and Matheson, Herbst and Holt (8 , 9) have treated the degree of segregation as a result of a dynamic balance between (*i*) the segregation tendency, or rate of separation of fluid from particles and (*ii*) the remixing tendency, or rate of gravity flow of particles into fluid pockets. Morse treated the segregation tendency as a fluid flow problem by applying the Carman equation for flow through fixed packed beds to adjacent zone in a fluidized bed and obtained the following equation ·

$$W_0 = \frac{L_f (\rho_s - \rho_f) . (\varepsilon_2 - \varepsilon_1) . g_c . \varepsilon_3^2}{\mu \; a^2 \qquad 5 . L_1} \qquad 5$$

The equation indicates that segregation is self-accelerating and is greater in deeper beds. Segregation is favoured also by large particle size and density, by large difference in density between particle and fluid and by small fluid viscosity.

Continuous fluidization.—Data on continuous fluidization are scarce The only two papers available on this in published literature are those

by Lewis, Gilliland and Bauer (10) and Valentine (14). The test apparatus used by Lewis and his co-workers consisted of 10 ft of $1\frac{1}{4}$ inches internal diameter brass tubing. Glass beads were introduced in the bottom of the section together with the fluidizing air. A cyclone separator at the top permitted return of entrained disperse phase to a solid feed standpipe. They determined the average solid density (or solid concentration) for different solid feed rates. The graph obtained by them is shown in Fig. 1 (*see page* 34). In the graph the steady and unsteady operation regions are also indicated. In the steady operation regions the experimental conditions could be maintained for a longer duration without any significant variations, also the density for a given solid feed rate decreased with increase in fluid velocity. In all cases the bulk densities obtained for a given solid were lower than those for batch fluidization.

Time of residence.—Parent, Yagol and Steiner (12) derived an expression for calculating the probable time of residence of a particle of fluidized solids within a reactor continuously operated. They considered a system of fluidized solids where fresh material was constantly introduced at a fixed rate, perfect mixing was taking place, and material was continuously withdrawn at such a rate as to keep a fixed quantity in the system. Assuming the rate of income of the originally present material as zero they derived

$$dm = 0 - n \frac{m}{m_0} d\phi \qquad 6$$

where dm is the increase in mass of 'tagged particles,' n is the rate of withdrawal of all kinds of particles in mass per unit time, and m/m_0 was the concentration of tagged particles per unit of total mass. Assuming the total at any time as the same as that originally present and substituting m_0/ϕ_H for n (where ϕ_H was the average holding time) equation 7 was rewritten as

$$-dm = \frac{m}{\phi_H} - d\phi \qquad 7$$

whence after integration

$$m = m_0 . e^{-\frac{\phi}{\phi}} \qquad 8$$

or

$$X = e^{-\frac{\phi}{\phi_H}} \qquad 9$$

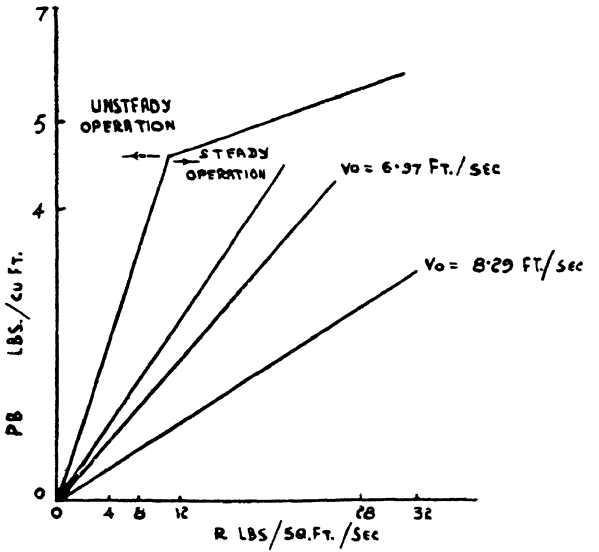


FIG. 1

SOLID CONCENTRATION IN FLUIDISED BED (PB) Vs SOLID FEED RATE (R) AT VELOCITIES Vo AND WITH PARTICLE DIAMETER 0·0016-INCH.

where X was the fraction of particles originally present that were still present in the reactor after time ϕ.

Head loss calculations.—Parent, Yagol and Steiner (12) also derived an expression for calculating the head losses in a fluidized bed by assuming that the head loss was due to (*i*) 'hydrostatic' or suspension head of the solid and (*ii*) the complex motions of the gas and particles.

If 'v' is the volume of the solid particles exclusive of voids, D is the inner diameter, and m and ρ_s are the mass and true density of the solids respectively, then

$$v = \frac{\pi}{4} D^2 . Z_o = \frac{m}{\rho_s} \qquad 10$$

or

$$Z_o = \frac{4m}{\pi D^2 \rho_s} \qquad 11$$

where Z_o is the hypothetical height of the void-free solid substance in the tube.

To obtain an head-loss expression in terms of manometer reading, Z_o is multiplied by the ratio of the densities of the solid and manometer fluid whence

$$Z' = \frac{4 . m}{\pi . D^2 . \rho_{fl}} \qquad 12$$

where Z' is the pressure drop expressed as manometer reading and P_{fl} is the density of the manometer fluid

Apparatus and Procedure

The apparatus used in these experiments is shown in Figure 2 (*see page* 36) The fluidizing column consisted of a 5ft pyrex tube one inch in diameter Static pressure readings were obtained from two taps located near the top and bottom of the column. Crushed coal is fed to the column through a screw conveyor driven by a geared electric motor, and is fluidized by air fed to the bottom of the column after duly being metered. The top of the column is connected to a cyclone

The procedure adopted was to determine experimentally the concentration of coal particles inside the fluidizing column at different air velocities and correlate them with those calculated from the corresponding pressure differential reading of the manometer For the experimental determination of solid concentration, a glass ball which

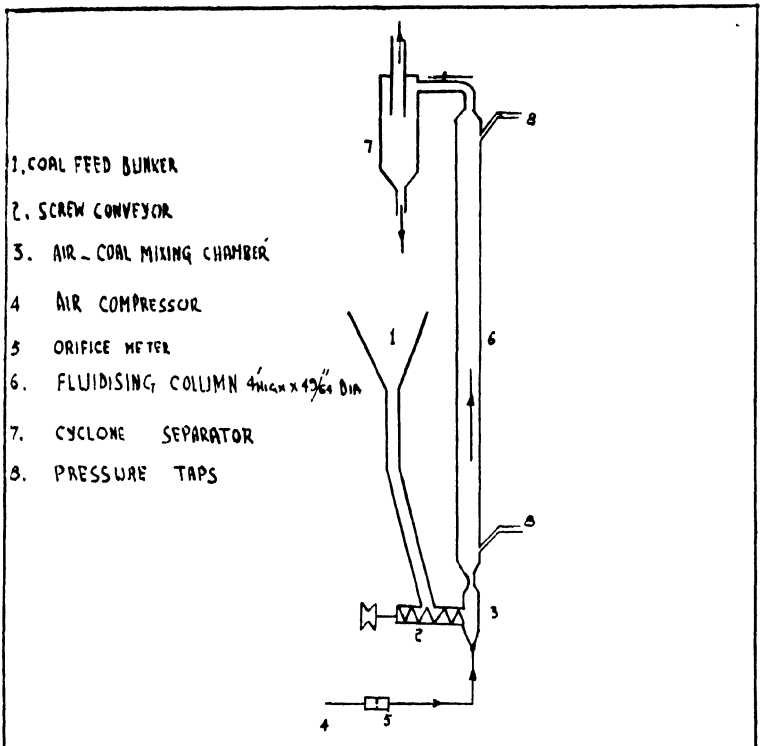


FIG. 2

APPARATUS USED FOR CONTINUOUS FLUIDISATION OF HYDERABAD COAL

could tightly fit on the conical portion of the tube at the bottom was used. This acted as a one-way valve allowing the coal-air mixtures to flow counter-gravity in the column but closing the gravity flow of the coal particles at any given instant when the air flow was suddenly closed.

Materials

Singareni coals were used throughout these experiments. The coals for the experiments were prepared by crushing egg-sized lumps to pieces of approximately 0.25 inch. The fragments were reduced still further in an edge-runner and passed through standard sieves.

Data

The data presented here deal with only coal of 60-100 mesh B S S and are presented in Table I. The experimental and calculated particle concentrations are plotted against the different air rates in Figure 3.

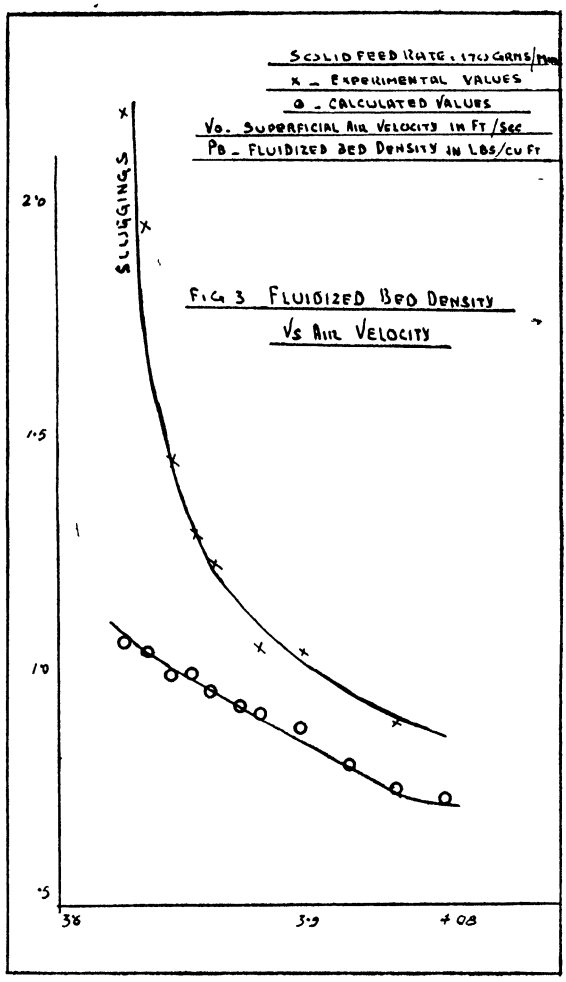


FIG 3 FLUIDIZED BED DENSITY VS AIR VELOCITY

TABLE I.

Data obtained with a fluidizing column of 0 7656 inches diameter and 4 ft height, using a constant feed of 170 grams per minute of 60-100 mesh B.S S. coal particles, varying the velocity of air

Run No	Superficial velocity of air flow, ft /sec.	Fluidized bed density, lb / cu ft	
		Calculated values	Expt. Values
1	4 083	0 726	0 888
2	4 017	0 753	0 900
3	3 962	0 807	0 993
4	3 907	0 888	1 039
5	3 852	0.914	1 054
6	3 823	0 927	1 086
7	3 796	0 955	1 226
8	3 767	0 987	1 297
9	3 739	1 008	1 449
10*	3 710	1 035	1 947
11*	3 681	1 062	2 194

* Slugging conditions

Discussion

As can be seen from Table I and Fig 3, the solid concentration is a maximum at low air rates and decreases as the flow of air is increased

Wilhelm, Morse, Matheson, Herbst and Holt have postulated a balance between (*i*) the segregation tendency, or rate of separation of fluid from particles into pockets, and (*ii*) the remixing tendency, to explain the quality of fluidization According to them aggregative fluidization results from a high segregation rate of a free flowing material and particulate fluidization, from a low segregation rate

In light of the work of Wilhelm and others, the results obtained by us can be interpreted as follows with increase in air rates the tendency for segregation of particles is reduced and the balance between segregative forces and dispersive forces tilts in favour of particulate fluidization resulting in a decrease in particle concentration in the column The same interpretation can be expressed differently as follows with increase in air rate the particles gather individual momentum and are carried out of the column resulting in the decrease of concentration of particles.

Acknowledgement

The authors want to take this opportunity of thanking Dr. Husain Zaheer, Director, Central Laboratories for Scientific & Industrial Research, for taking a keen interest in these investigations and for permitting this paper to be presented at the symposium.

Nomenclature

A_T = cross-sectional area of fluidization vessel, (sq.ft.)

D_p = diameter of sphere of the same volume as that of the particle, (ft.)

g_c = conversion factor, 32.17 (ft.) (lb)/(lb. force) (sec)^2

g = local acceleration due to gravity, (ft)/(sec)^2

G = superficial mass velocity (based on gross cross-sectional area of empty tube), (lb)/(sec) (sq ft)

G_e = mass velocity for expansion of bed, (lb)/(sq ft.)/(hr.)

G_f = mass velocity for fluidization of bed, (lb)/(sq ft)/(hr.)

G_{mf} = mass velocity of fluid required to lift a bed at minimum fluid voidage, (lb)/(sq ft)/(hr)

L = height of settled bed (or length of pipe), (ft.)

m = exponent on $\frac{\varepsilon^3}{(1-\varepsilon)^2}$ in Leva's fluidization correlation (dimensionless)

n = exponent on Reynolds number to correlate with friction factor, (dimensionless)

Δp = pressure drop, (lb.)/(sq.ft.)

L_f = height of fluidized bed, (ft.)

$L1$ = length of the flow path between segregation zones, (ft.)

a = surface area of particles per unit volume of packed space (sq.ft.)/(cu.ft.)

u_o = superficial velocity of fluid through the bed, (ft.)/(sec.)

ε = fraction of voids in the bed of particles, (dimensionless)

$\varepsilon_1 \varepsilon_2$ = average fractions of voids in columns above two neighbouring zones, 1 and 2

μ = fluid viscosity, absolute, (lb.)/(ft.) (sec.)

ρ_f = fluid density, (lb. mass)/(cu.ft.)

ρ_s = true (not bulk) particle density, (lb. mass)/cu.ft.)

λ = particle shape factor, (dimensionless)

ϕ = fluidization efficiency, (dimensionless)

f = modified friction factor $= \dfrac{\Delta p\, D_p\, \rho_f\, g}{2\, G^2 L} \dfrac{\varepsilon^3}{(1-\varepsilon)^2}$

V_T = dumped volume of packed material in column, (cu.ft.)

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(*Sunday, 13th August*, 1950)

DISCUSSION

Participants :

1 Dr H G Kayser, Laxminarayana Institute of Technology, Nagpur (Chairman)

2 Dr S Husain Zaheer, C. L S I R, Hyderabad-Dn.

3 Dr M R Mandlekar, Commerce & Industries Department, Bombay.

4 Dr M. S. Iyengar, C L S I R., Hyderabad-Dn.

5 Dr M G Krishna, C L S I R, Hyderabad-Dn

6. Mr. G Satyanarayana Rao, C. L. S I. R., Hyderabad-Dn.

7. Mr. S. S. Ghosh, Indian Institute of Science, Bangalore.

The importance of *Particle size* and the *quantity of fluidizing medium* in processes using fluidization was stressed by a number of speakers (M.R.M., S.S.G., M.G.K.) Just as a particular quantity of air is required per pound of oil in oil burners, and air for gasification of per pound of coal, it is necessary to know whether the quantity of gas required to fluidize coal is more than that required for the actual gasification reaction ; for if this is so it would increase the cost of production (M R M) The paper under discussion being a report of preliminary investigations of fluidization of coal does not include this data (M S I) However, data of this kind are necessary in the proper design of a gasification plant (S.S.G., M.G.K.).

The *bulk density (or solid concentration)* in a fluidizing column is another important factor which has to be taken into consideration In the data presented in the paper under discussion, the bulk densities obtained for 60-100 mesh B S.S , (M S.I) in a 1 - inch column varied between 0.6-2 lbs. cu. ft for air flow ranges of 3-4 ft sec. (G.S.R.) In experiments carried out at Bangalore on a 5-ft. column, heated externally to 900°C. and having a 1 - inch diameter, when coal was fed from the top through an annular space between a conical hopper and a central rotating shaft, the fluidizing gas (pre-heated nitrogen) entered the column from the bottom and when the gaseous products were taken out from a gas exit placed slightly below the solid feed hopper, it was found that a bulk density of 5 5 lbs. / cu ft was obtained. Lewis, Gilliland and Bauer had obtained bulk densities as high as 10 lbs. / cu ft. in their experiments which they considered as ideal for efficient gasification (S.S G) However, it was doubted (M S.I.) whether the conditions obtained by counter-current flow of solid and fluid could be called fluidization and also whether such high bulk densities of coal were needed for efficient gasification as the quantity needed depends on the type of fluidizing column used (M S.I.) It was however contended (S S.G.) that even though there was counter-current flow in the apparatus worked at Bangalore, the process could still be called fluidization as there was thorough mixing of gas and solid in the column and as the solids were in suspension. A doubt was expressed (M G.K) whether such high bulk densities could ever be obtained in a 1 - inch fluidizing column. Besides, bulk density did not merely depend on solid feed rate and gas feed rate There were other factors like the densities of the solid and the fluid, the diameter and shape of the column, and the particle size which also were to be considered (M.G K.).

An opinion was expressed (H.G.K) that the equation $\phi = \frac{G_F - G_e}{G_F}$ presented for calculating *the efficiency of fluidization* was inadequate and might not represent the true efficiency of a fluidization process , for as the expression stood, large values of G_F were needed for achieving cent percent efficiency It was however felt (M G.K) that the expression did not represent the overall efficiency of a process. The equation merely represented the energy spent in expanding the bed before it could actually be fluidized In fact the equation should have been presented as $\phi \frac{W^1 - W_E}{W_T}$, where W_T – total energy for expansion and fluidization of the bed, and W_E – energy spent merely in the expansion of the bed The equation presented only gave an indication as to the proportion of work done in merely expanding the bed compared to that required for fluidizing the bed (M G K)

Another factor to be taken into account in fluidization processes was *the time of residence* of solid particles in the fluidizing column The efficiency of reaction depended on the time for which the particle stayed in the reactor There was a danger in fluidization that the particles might fly off the column even before they had time to react and as a result the efficiency of the process might be reduced (H.G K) However this might be a danger only in continuous fluidization processes The time of residence of the solid particles depended on the height of the column and the velocity of the particles By a careful control of the two variables the time of residence of the particles in the column could be adjusted (M G K)

It was necessary in fluidization experiments to obtain data on *heat transfers* (S S G.). The experiments carried out in Germany on fixed beds indicated that the heat transfer was more in the case of fixed beds than in the case of fluidized beds though heat distribution was more equitable in the case of the latter (H G K) However, it was felt (M.G K)that such comparisons would have to be made carefully taking into account the method of heating (whether external or internal) and the time factor It would seem that the time taken to attain maximum temperature would be less in the case of a fluidized bed than in the case of a fixed bed.

In the application of fluidization processes to non-catalytic reactions like those of gasification of coal one of the difficulties encountered was in

maintaining the particle size in the reactor throughout the process (M.S.I). As the reaction proceeded the particles got consumed thereby upsetting the conditions of fluidization. Another difficulty encountered was that while using caking coal, at one stage of the process, due to the agglomerating tendency of the coal, the particles stuck to one another resulting in the collapse of the fluidized bed (M S I) Yet another difficulty would be encountered (H G K) by the segregation tendency of the ash as the reaction proceeded In Germany, experience with the Winkler gas generator had shown that though the gas producer had a high capacity it had a low efficiency Also in one of the plants it was noticed that the 'carry-away' in the gas stream of coal or coke amounted to as much as 40 per cent of the total fuel used. Also, due to the segregation tendency of coal-ash and difference in the densities of coal and coal ash, the latter might tend to fall upsetting fluidization (H.G K.). The settling of ash particles however depended on the size, density and free falling velocity, and by maintaining the velocity of fluidizing gas slightly higher than the free falling velocity of ash, and lower than that of coal particles, the settling tendency of ash in a fluidized bed could be overcome (M G K). The difficulty of maintaining the particle size always throughout the reaction, the agglomerating tendency of caking coals, and other difficulties ensuing from it could all be overcome by recirculating part of the ash and thus compensating for the change in particle size, as was being done in Australia in the industrial scale operation of shale-oil plant using fluidization (M S I).

CRACKING OF HEAVY PETROLEUM RESIDUES IN CONTACT WITH COAL

by

MR. G. RAMA RAO

(Osmania Technical College, Hyderabad-Deccan)

The Knowles' process for utilising heavy petroleum residues for the production of coke from non-caking coals and gas is modified. In the modified process the coal is first carbonised at a temperature of 600°C. in a Mansfield retort and the crude oil is allowed to trickle in a thin stream over the hot soft coke in the retort. A residue resembling metallurgical coke is obtained.

The Knowles' process, originally designed and developed in the U.S.A., is used for :

(1) handling the heavy residues from the cracking of petroleum,

(2) producing coke from non-caking coals, and

(3) utilising the tars and pitch from the carbonisation industries.

Heavy residual oils like fuel oils and heavy crudes of high Conradson carbon (ranging from 5 to 14) when run into an oven and allowed to stand at 950°F until coking is complete, yield a large percentage of good ashless petroleum coke and gas oil. If the time of contact is reduced, the products contain larger amounts of gasoline and gas On cracking heavy crude oil in a Mansfield gas producer, the following products were obtained :

Weight of oil cracked	36 lbs
Volume of gas produced	331 cu. ft.
Weight of gas oil collected	6 lbs.
Calorific value of gas	1450 B Th.U.

In the Osmania Technical College the above oil is used for gas making and is found economical.

In the second process for the production of metallurgical coke from non-caking coals, equal quantities of coal and oil by weight are mixed and carbonised at 1000°C and the following are the yields :

Weight of coke	48 per cent	of total blend
Middle oil	24 ,,	,,
Heavy oil	8 ,,	,,
Gas	5 ,,	,,

The middle oil on further cracking produced 35 per cent raw gasoline and 60 per cent residual oil which is used as feed in the process. The process has been modified. Instead of mixing the coal and oil, the coal is first carbonised at a temperature of 600°C. in a Mansfield retort and the gases are cooled in an oil cooler and scrubber. The temperature of the residue in the retort is raised to cherry red heat and the crude oil is allowed to trickle in a thin stream over the soft coke. The results obtained were as follows :

Weight of coal in the retort	20 lbs.
Weight of oil cracked	26 lbs.
Oil recovered by stripping the scrubber at 250°C.	1·4 gallons
Sp. gravity of the oil	0·8
Colour of the oil	yellow
Volume of the distillate obtained from the oil at 170°C	0·7 gallons
Colour of the distillate	pale yellow

The residue in the retort is hard and lustrous and resembles very closely metallurgical coke in its burning property.

Another set of experiments was tried in which the coal was first carbonised in a horizontal metallic tube 2 inches in diameter and 28 inches long. One end was fitted with with a fuel injector worked by a high pressure ram pump operating at a pressure of 100 atms. The other end of the tube was connected to a water cooler and two oil scrubbers. After completing carbonisation at 600°C the residue was raised to a temperature of 900°C. and oil was sprayed over it at regular intervals. The results obtained were as follows :

Weight of coal taken	1 lb.
Volume of oil sprayed	200 ml
Weight of residue	0·812 lbs.
Volume of oil obtained from scrubber	90 ml.

The coke obtained was not as hard as in previous experiments.

(*Wednesday, 16th August,* 1950)

DISCUSSION.

Participants.

1. Dr. H. G. Kayser, Laxminarayana Institute of Technology, Nagpur. (Chairman)
2. Dr. B S Kulkarni, Applied Chemistry Department, Osmania University, Hyderabad-Deccan.
3. Dr. M. R. Mandlekar, Commerce & Industries Department, Bombay.
4. Mr. S S Ghosh, Indian Institute of Science, Bangalore
5. Dr. S. Husain Zaheer, Central Laboratories for Scientific & Industrial Research, Hyderabad-Deccan
6. Dr. M S Iyengar, do do
7. Dr M. G Krishna, do do
8. Mr G Rama Rao, Osmania Technical College Hyderabad Dn

Replying to some general questions regarding the *purpose of the experiments* (H G.K), *nature of the oil used* (S.H Z), *size of the coal used* (H G K), *ash contents of coal used* and coke obtained (B S K) and *methods of heating* employed, the speaker (G R R) explained that the main idea behind the effort was that of converting non-caking coal into hard metallurgical coke suitable for foundry purposes, oils being also recovered from the cracked products The residual fraction (Conradson value 12, boiling point 350-370°C) left behind after the recovery of high-speed diesel oil for use in transport vehicles was obtained for use from the local Road Transport Department workshops , the coal used had an ash content of 20- 28 percent , and varied from 3/4" to 2" in size, the tube had been externally heated by gas The resulting coke had not been analysed for ash content

The suitability of such coke for mettallurgical purposes was doubted (M R. M) since the material balance indicated a probable high ash content , in fact the product, strictly speaking, could be called gas coke but hardly metallurgical coke In reply the speaker (G R R) stated that the probable ash content of the coke was a value 1 ½ times that of the coal used, *i e* , it would work out at about 32-34 percent It was probable that this coke could not be used in blast furnaces (though this had yet to be tested in practice), but it could be used in foundries and workshops, and the aim of the process had been merely to give hard coke from non-caking coals

The hardness of the coke obtained came in for some comment The coke was hard enough to resist breakage during transport, the speaker (G R R.) said. Very hard coke had been obtained from Bellampalli

(Hyderabad) coals in the course of low-temperature carbonisation studies at Leeds (M.S.I.) which was hard enough for use in cupolas and had been shipped undamaged from England to Sweden for trial in electric furnaces, from the same Bellampalli coal, the firm of Lurgi had obtained hard coke by carbonisation at 600° C. Several speakers (G.R.R., S.S.G.) contended that in their own experience low-temperature carbonisation had always yielded a spongy coke that could not be conveyed without breaking even a few hundred yards, this was possibly due to differing methods of working the carbonisation process, especially in regard to methods of quenching (dry quenching had been used in the experiments described in the paper) and in starting materials (moisture content, etc.) (M.S.I.), it was known that coke with a moisture content of over 6 percent was unsuitable for use in cupolas (G.R.R.).

Possible modifications of the process used by the speaker were pointed out. The hardness of the coke probably resulted from the binding property of the tar formed inside the furnace tube during cracking of the oils; would not better control result if the oil were cracked separately and the resulting tar allowed to trickle over the coke (B.S.K.)? The speaker (G.R.R.) pointed out that such a procedure - the known Brassert process—was in two stages which in the present process had been economically combined, the cracking of the oil on the coke could be controlled and did not interfere with the subsequent binding of coke. Another suggestion (M.R.M.) was that anthracene oil, at present wasted, might replace the imported diesel oil residue used in the process; this was possible, but the diesel oil residue used was itself a waste product (G.R.R.). It was agreed that large scale trials on a Mansfield plant could most usefully be conducted, and the economics of the process worked out in detail (M.G.K.).

The Chairman (H.G.K.), *summarising*, was of opinion that the process described in the paper that had been read, though based on a good idea, necessitated the destruction of valuable materials like diesel oil, and this he did not favour. The process combined low-temperature carbonisation and briquetting, but this advntage was more than overshadowed by the losses incurred in the break-down of valuable materials, though judgment on this point would have to await the computation of commercial-scale working-costs. He had one suggestion to make that a continuous process should be sought for, with consequent gain in economy, in line with the general emphasis in any industrial process today.

NEED FOR RESEARCH ON REFRACTORY MATERIALS

by

MR. ABDE ALI

(Department of Applied Chemistry, Osmania University, Hyderabad-Dn.)

I. Introduction.

The term "refractory material" signifies any non-metallic material capable of withstanding elevated temperatures, without destruction or deterioration (by fusion, sublimation, chemical decomposition or physico-chemical transformations) so rapidly as to preclude its use in the construction of vessels, linings, furnace walls, flues, etc, subjected to high temperatures. Although resistance to high temperature is the primary and distinguishing characteristic demanded of refractory materials as a class, almost every refractory employed in modern industry must also exhibit, while at a high temperature, an adequate resistance towards one or more of the following destructive agents (1) pressure or load, (2) mechanical vibration, (3) frequent, rapid and unequal heating or cooling, or any one or more of these, (4) the stresses set up by expansion or contraction of other parts of the furnace or vessel of which the refractory material is a component part, (5) mechanical abrasion by ashes, cinders, etc, or by the furnace charge itself; (6) the chemical action of atmospheric and furnace gases, (7) the slagging action of the furnace charge or of the materials given off by it; and (8) the chemical action of any other furnace parts such, for example, as the electrodes or the heating element in an electric furnace; and in certain special cases the refractory must (9) while at high temperature (*a*) remain a good electrical insulator or (*b*) become an electrical conductor or (10) (*a*) remain a good thermal insulator or (*b*) to a given degree become a thermal conductor.

Every industrial plant which employs high temperatures in any part of its work has a more or less acute problem of refractory materials to deal with. The refractory material employed may vary in type all the way from ordinary fire bricks (such as are employed in the boiler settings of the power plant) upto highly specialized materials designed to withstand one or more of the special destructive agents mentioned

above. Railway locomotives and the power plants of ships can be operated with the highest efficiency only when properly designed refractory materials are used in their construction Practically all the metallurgical industries, both those which have to do with extraction of metals from ores as well as those engaged in working the various metals or preparing alloys, have especially trying and difficult refractory problems to meet An important part is also played by refractory materials in the manufacture of electric furnace products (such as abrasive materials, graphite, carbide nitrogen products from the air, and a variety of other chemical products) , of glass and quartz articles , of lime, cement, potash, fuel gas, ammonia, coke, and many of the pigments , and of course of all ceramic products

As a field for industrial research, the subject of refractory material is, therefore, fundamental in character, widespread in its practical applications and of great national importance The present trend of many industries in the direction of using increasingly high temperatures in their operations is a further indication of the growing importance of a thorough and systematic scientific investigation of the various problems connected with the preparation and use of refractory materials.

In a high temperature furnace or kiln, where the internal temperature required is higher than the refractory lining will withstand, it is customary to protect this lining by artificial cooling either by means of air or water. Such artificial cooling naturally results in a great waste of heat and in a corresponding greater consumption of fuel The ideal arrangement would be to cover the outside of the furnace with a good thermal insulator so as to retain this heat in the furnace, but in many cases under present conditions such an insulation would result in the rapid destruction of the refractory lining, owing to the fact that this lining would soon attain the temperature of the inside of the furnace. It is obvious that the development of refractory materials which would permit the thermal insulation of industrial furnaces would result in an enormous fuel saving, since the wastage resulting from present methods is one of the large elements in the total fuel consumption of industrial furnaces. Perfect adaptation of the refractory to furnace conditions (temperature, pressure, chemical action, mechanical abrasion, etc) is one of the big problems whose successful solution would constitute a great contribution to the fuel conservation movement.

II. Annual Production and Consumption of Refractory Materials in India.

Statistics on the annual production of refractory materials and products in India do not seem to be available in public records. Tata's Iron and Steel Works alone consume Rs. 50,00,000/- worth of refractories annually The total consumption of refractories by the following Industries will easily add up to many millions of rupees.

1 The Iron and Steel Industry.
2 The various non-ferrous metal industries
3 The gas industry
4. The by-product Coke industry
5 The Glass industry
6 The Pottery and Porcelain industries.
7 The Brick, Tile and Sewer Pipe Industries.
8. The Cement Industry.
9 The various industries employing Electric Furnaces.
10 The Enamelling industries.
11 The great variety of Chemical Industries employing high temperatures.
12. Power Plants.

About 90 percent of the refractory in Industry seems to be concentrated in the North-East of India.

Some of the leading refractory manufacturers are the following :—

(1) *The Kumar Dhobi Fire Clay and Silica Works* :—These are about the biggest refractory manufacturers in the country. They have a Fire Clay Department which is 50 years old and a Sillimanite and Silica Department Magnesite Bricks were made during the war but their manufacture was discontinued due to heavy pressure of orders for Silica and Sillimanite Bricks. The capacity of the plant is 50,000 tons per year Out of this 60 percent of the production comprise Fire Clay and bauxite refractories and 40 percent Silica and Sillimanite.

(2) *Messrs. Burns and Co., Ramguny* —They manufacture both fire clay and special refractories such as silica, magnesite, sillimanite and chromite.

(3) *Reliance Fire Brick and Pottery Co , Ltd , Barakar* —This firm, besides the pottery section, manufactures fire clay refractories, refractory mortars and cement. The capacity for refractories production is 40,000 tons per year.

(4) *Bihar Fire Clay and Potteries, Ltd., Mugma* —Make fire clay refractories to the extent of 30,000 tons per year.

(5) *Messrs. Bird & Co.*

(6) *Refractories plant of the Tata Iron and Steel Works, Ltd , Jamshedpur.*

(7) *Refractories plant of the Bhadravati Iron & Steel Works, Ltd , Bhadravati, Mysore.*

(8) *Bengal Fire Brick Co., Burdwan.*

(9) *Jubbulpore Pottery Works, Jubbulpore.*

(10) *Katni Cement and Industrial Co , Ltd , Katni*

(11) *Kolar Brick Making Co., Ltd , Kolar, Mysore.*

The location of minerals of ceramic importance from which refractories can be produced in India are given in Table 1 *(see page 52)*

III. Recent developments in high-temperature refractory materials.

Before discussing the various aspects of the subject of refractory materials as a field for research, it is desirable to review recent developments in high temperature refractory materials, as these developments not only emphasise the need for research but also indicate the lines on which additional work is to be conducted , the review is confined to a few refractory materials of very high refractoriness

Fused Magnesia -

Until the X-ray technique was used to study the nature of magnesium oxide crystals it was believed that there were two crystalline forms, one of low density and the other of high density, the former changing into the latter when heated at a sufficiently high temperature for a sufficiently long time About 12 years ago it was found that the X-ray pattern of magnesium oxide is fundamentally the same whatever the crystal size or apparent density This was an important finding, for it showed by inference that the properties of pure magnesia refractories must be greatly influenced by the crystal size of the periclase, *i e*, the crystalline magnesium oxide.

TABLE I.

DISTRIBUTION OF REFACTORY ROCKS, CLAYS

Name of the mineral, etc.	Assam	Bihar	Bombay	Central India	Central Provinces
1. Bauxite		Palamau Ranchi	Belgaum Satara Surat Kaira Kohlapur Ratnagiri		Balaghat Jubbulpore Mandla Seoni Bilaspur Sarguja Jashpur
2. Beryl		Hazari Bagh Monghyr			
3. Chromite		Singbhum	Ratnagiri		
4. Corundum	Nongstoin	Manbhum Singbhum Hazari Bagh Monghyr		Rewa	Bhandara
5 Graphite		Palamau Monghyr			
6. Kaolin	Lakhimpur Garohill Bankura Burdwan Darjeeling	Bhagalpur Manbhum Santal Parganas Singbhum	Rajpipla	Gwalior Rewa Sohawal	Jubbulpore Raipur

Hyderabad	Madras, Mysore, Travancore	Orissa	Punjab & Kashmir	Rajputana Delhi	United Provinces
	Madura Nilgiris Vizagapatam Mysore	Kalahandi	Simla Jammu Paikhet	Jahlawar Tonk	
	Nellore Coimbatore Bangalore	–	Kashmir	Kishengarh Ajmer Jaipur	
	Salem Hasan Mysore		Kangra Ladakh		
Warangal	Anatapur Coimbatore S Kanara Salem Bangalore Hasan Mysore	Cuttack	Padar Kashmir	Jaipur	
Warangal Karimnagar	Godavari Tinnevelly Vizagapatam Travancore Mysore				
Nalgonda	Arcot, Nellore Nilgiris Mysore Kodur Bangalore Madras, etc.	Cuttack Puri Mayurbhanj	Kashmir	Ajmer Jaipur Delhi	

Continued on page 54

TABLE I. (Cont.)

DISTRIBUTION OF REFACTORY ROCKS, CLAYS

Name of the mineral, etc.	Assam	Bihar	Bombay	Central India	Central Provinces
7 Kyanite		Singbhum Man-bhum		Rewa Maihar States	
8. Limestone	Khasi Jaitia Hills	Rohtas-garh	Porban-dar		
9. Magnesite			Idar		
10. Monazite			Sabar-mati R. Idar		
11. Quartzite		Gaya			
12. Sillimanite	Nong-stoin	Monghyr		Rewa	Bhandara
13 Titanium minerals		Man-bhum Singbhum			
14 Uranium minerals		Gaya			
15. Wolfram		Singbhum			Nagpur
16. Zircon					

Hyderabad	Madras, Mysore, Travancore	Orissa	Punjab & Kashmir	Rajputana Delhi	United Provinces
Warangal	Nellore Coimbatore Mysore		Patiala	Kishengarh Ajmer Mewara	
				Sojat Bilara Gotan Bundi States Sirolu	
	Salem Kurnool Bellary Coorg Trichinopoly Mysore Hasan		Kashmir	Ajmer Dungarpur Mewara	
	Travancore Bangalore				
		Bamra			
	Trichinopoly Travancore		Kashmir Patiala	Alwar Kishengarh	Mirzapur
	Nellore				
	Trichinopoly			Jodhpur	
	Travancore Coimbatore				

The growth of periclase crystals and its importance as a factor determining the behaviour of magnesia refractories, has been discussed by Colegrave, Richardson and Rigby[2]. They observed that periclase crystals, formed as a result of firing at normal kiln temperatures for comparatively short periods, are usually rounded , when reheated at a higher temperature the crystals increase in size and one or more cleavages are formed ; if the heat treatment is sufficiently intense, well defined cleavage cracks are formed in two directions Crystal growth is, of course, greatly affected by the presence of impurities . it has been known that the ferruginous Austrian magnesite shrinks (owing to recrystallization) more rapidly than does the purer magnesite from Greece. It is now considered that iron oxide may act as a mineralizer through the formation of solid solutions, but this explanation will not serve when the effects of silica and lime which behave similarly to Fe_2O_3 are considered.

The results obtained by Colegrave, Richardson and Rigby (*loc. cit.*) on the increase in crystal size with increasing firing temperature are shown in Figure 1 ; the influence of iron oxide on crystal growth is also shown An increase in temperature of firing from 1,350°C to 1,450°C. increased the crystal size about eight fold ; at a given firing temperature crystal size was markedly increased if ferrous oxide was present. The same authors reported the results of shrinkage measurements ; these are reproduced in Figure 2. The curve clearly shows the close relationship between shrinkage and crystal growth

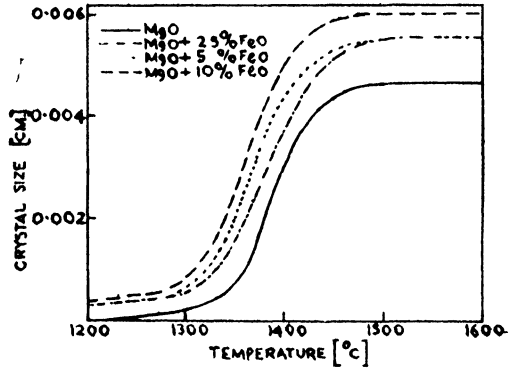

FIG. 1.—EFFECT OF FIRING TEMPERATURE AND IRON OXIDE CONTENT ON THE CRYSTAL SIZE OF MAGNESIA.

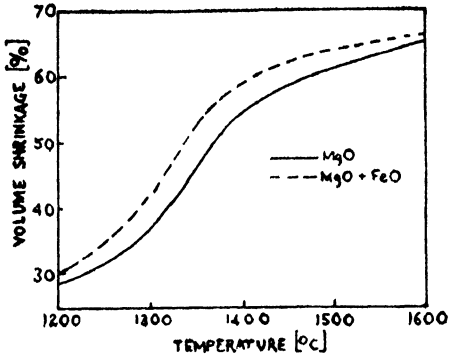

FIG. 2.—EFFECT OF FIRING TEMPERATURE AND IRON OXIDE CONTENT ON THE SHRINKAGE OF MAGNESIA.

For some purposes a disadvantage of magnesia as a refractory is its high thermal expansion (about 1·3 percent between 0 and 1,000°C). High thermal expansion is one cause of low resistance to spalling. An Austrian magnesite brick, "Radex A," with improved spalling resistance, was made before World War II[3], it contained 4 to 6 per cent. Al_2O_3, which was present as spinel. It was formerly believed that the high spalling resistance was due to the ability of these bricks to take up stresses by slip along their well developed cleavage planes. More recent work has led to a revision of this hypothesis; micro-examination of the texture has led to the conclusion that the high spalling resistance of "Radex A" bricks is a result of the grading and the presence of the spinel. The importance of grading has recently been demonstrated by Ford and Rees[4].

Fused Alumina :—

Pure alumina exists in two forms. The low-temperature form, gamma-alumina, is converted to the high temperature form, alpha-alumina (corundum), by heating at any temperature above 1,100 to 1,200°C. The change from the gamma- to the alpha-form is irreversible.

An important feature of corundum is the way in which it sinters. The pure oxide melts at about 2,030°C. but if a compact test-piece of the material is fired at 1,600 to 1,700°C., it becomes quite strong, also it shrinks very considerably. The sintering and shrinkage result from

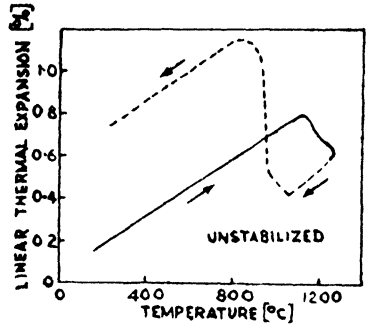

FIG. 3.—THERMAL EXPANSION OF UNSTABILIZED ZIRCONIA.

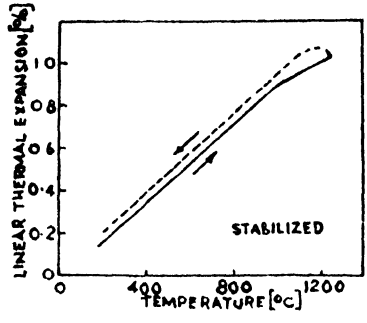

FIG. 4.—THERMAL EXPANSION OF STABILIZED ZIRCONIA.

intercrystallization and growth of the corundum. The effect is explained by the physical-chemist in terms of free surface energy ; the very small crystals have a higher surface energy than the larger crystals and there is a state of disequilibrium Equilibrium is brought about by the joining together and growth of the more highly energized small crystals. It has been stated that heating at 1,900°C. for 2 to 3 hours results in the growth of corundum crystals to about ten times their original size. The appreciable vapour pressure of alumina at this high temperature is contributory to the crystal growth, the surface atoms evidently being in a state of high mobility , the vapour pressure of alumina increases from a few millimetres at 1,700°C to 200 mm. at 2,100°C

A difficulty in the production of alumina ware is the control of the orientation of the crystals Production methods, whether by casting from a slip or by extrusion of a paste, tend to give a preferred orientation to the crystallites in the unfired ware. In addition, corundum crystals tend to grow more quickly in the direction of their c-axis.

It has recently been shown[5], however, that the fracture of well-sintered corundum bars takes place through the crystals almost as readily as by way of the crystal boundaries , moreover, the transverse strength of a well-sintered polycrystalline bar is scarcely inferior to that of a single corundum crystal.

TABLE 2.

MECHANICAL PROPERTIES OF FUSED ALUMINA[6]

Temperature °C.	Tensile strength lb./sq in.	Crushing strength lb./sq in.	Elasticity modulus (X 10^7 lb./sq.in.)
20	37,000	420,000	5–6
1,000		126,000	4 5–5 5
1,300	6,500		3–4
1,500		14,000	

The strength of fused alumina products at room temperature is remarkably high, but falls rapidly at high temperatures. Some figures published in Germany during the war are given in Table 2 In spite of the very marked decrease in strength at high temperature, fused Al_2O_3 has valuable properties The results obtained for the modulus of elasticity were found to vary according to the diameter of the test piece.

A more important factor, however, was found to be the purity of the alumina, when 5 per cent. of silica was present, the modulus of elasticity at 1,300°C was about 2.5×10^7 compared with 3.5×10^7 for the pure oxide. The modulus of elasticity is one of the factors that determine spalling resistance. For a homogeneous material, the resistance to spalling (R) is given by the expression below, where

H = Strength
K = Thermal conductivity
Δ = Coefficient of expansion
E = The modulus of Elasticity
d = Density
C = Specific heat

$$R = \frac{M}{\Delta E} \sqrt{\frac{K}{dC}}$$

The strength factor depends on whether the material is being subjected to tensile or compressive stresses. Alumina has a high mechanical strength and thermal conductivity—both factors in its favour—but a high expansion and elasticity—factors to its disadvantage. Like all other refractories, however, it has a much reduced elasticity at high temperatures and is more resistant to spalling if the thermal shock remains within a high-temperature range.

Zirconia.—

The technology of silica refractories is dependent to a quite considerable extent on the polymorphism of silica. It was not generally realised, until comparatively recently, that this is also true of zirconia. Zirconia occurs naturally as baddeleyite and, as would be expected, the crystal form of baddeleyite (monoclinic) is that which is stable at normal temperatures. Monoclinic zirconia is stable up to about 1,100°C (the temperature appears to vary from sample to sample and according to the conditions of heating). At higher temperatures the stable form is tetragonal. The change from monoclinic to tetragonal zirconia is accompanied by a large change in volume, and the change is reversible, it is therefore akin to the alpha-beta quartz change, rather than to the conversion of quartz into cristobalite. There is also a trigonal form of zirconia.

The effect of this crystalline inversion is best seen in thermal expansion curves, Fig. 3 shows the linear change when zirconia is heated

to about 1,200°C and then cooled. Using pure oxide (98 8 per cent ZrO_2) it has been found that the overall change in length, *i e*, the change from the most contracted to the most expanded length, is of the order of 0 8 per cent[7] The expansion on cooling takes place more suddenly than the contraction on heating but the change can be repeated indefinitely.

In the silica brick industry the inversions of silica have had to be accepted; no method has been found to prevent them taking place. With zirconia, however, it has been found that a cubic solid solution rich in zirconia can be formed by firing the oxide with certain other refractory oxides Some of the results obtained at the National Bureau of Standards, Washington, D C, U S A, in an investigation of this problem are summarized in Table 3[8]. In this table the expansion coefficients

TABLE 3.

EFFECTS OF ADDITIONS ON THE EXPANSION OF ZIRCONIA

Composition		Expansion Coefficient		
ZrO_2	Additions	Firing Temperature, °C	Temperature range, °C	Coefficient (X 10^6)
100 per cent		1,465	20–1,000	7 7
			1,350–1,050	13 0
94 per cent	. 5 per cent CaO	1,700	30–1,230	10 7
			1,400– 100	11 5
92 per cent	. 6 per cent MgO	1,850	1,400–1,450	13 2
			1,000– 100	9 4
92 per cent	8 per cent Y_2O_5	1,850	700–1,400	10 9
			1,500– 600	12 8

are recorded, first as the value on heating in the given temperature range, and secondly as the value on cooling through a second temperature range Pure zirconia has a moderately high expansion up to 1,000°C but when cooled between 1,350°C. and 1,050°C. it has a still higher coefficient. The addition of 5 percent of lime followed by drastic firing (1,700°C.) results in the formation of a cubic solid solution which has a uniform expansion. Yttria also is effective, but not

magnesia (except at temperatures below 1,200°C.). A tentative explanation of the different behaviour of the added oxides is that their effect is in some measure proportional to their ionic radii ; the Ca-ion is 72 per cent bigger than the Zr-ion and quite a small proportion (5 per cent) stabilizes the cubic form ; the Mg - is 12 per cent smaller than the Zr-ion, and even an addition of 15 per cent of MgO is incapable of stabilizing the cubic solid solution BaO also has been reported to be effective as a stabilizing agent

The significance of these volume changes lies in their effect on the spalling resistance of zirconia. Even stabilized zirconia has a relatively high thermal expansion, however (see Fig 4) , this oxide also has a low thermal conductivity, so that any temperature difference caused by sudden heating or cooling is not quickly equalized, and hence stresses are readily set up when zirconia is subjected to thermal shock.

Zircon .—

With the discovery and exploitation of the beach sands in which heavy minerals have been concentrated in the course of geological time, zircon (*i.e*, zirconium silicate, $ZrSiO_4$) has become a readily available, though still expensive, mineral As a refractory, zircon has been found to have excellent resistance to attack by coal ash and by molten aluminium ; there are no doubt other spheres in which zircon could be used with success. Zircon, however, dissociates at about 1,600°C. into zirconia and free silica. Yet these refractories can be used at temperatures up to about 2,000°C. although the silica begins to volatilize. Some properties of zircon bricks are given in Table 4.

TABLE 4.

PROPERTIES OF ZIRCON BRICKS

Percentage composition	. ZrO_2	.. 60–65
	SiO_2	. 30–35
	TiO_2	0 5–5
Specific gravity	. 4.6	
Thermal expansion	. $4\ 5 \times 10^{-6}$	
Thermal conductivity	About 0 005 c g.s.	
Spalling resistance	.. Very good	

The thermal expansion of zircon is of the same order as that of a sillimanite brick and, largely in consequence of this, the spalling resistance is very good.

Beryllia.—

The major source of beryllium oxide is the mineral beryl ($3BeO.Al_2O_3.6SiO_2$) which occurs in felspar deposits in India, Brazil, Argentine and the U S.A. To extract the beryllia, the ore is heat-treated and is then leached with hot sulphuric acid.

The melting point of beryllia is higher than that of alumina but lower than that of magnesia, the approximate value is 2,550°C, but under certain conditions the oxide is volatile at much lower temperatures (the fumes are highly poisonous). On account of its uniform and moderate thermal expansion and its high thermal conductivity (intermediate between that of silicon carbide and that of magnesite) beryllia has very good resistance to thermal shock The bonding of beryllia ware takes place by a process of crystallization ; quantitative results obtained on this process by electron microscope measurements are given in Table 5.

TABLE 5

CRYSTAL GROWTH OF BERYLLIA[9]

Firing Temperature, °C	Crystal size, μ
1,200 ..	0 05 – 0 2
1,300 .	1 – 2
1,400 ..	2 – 4
1,500 ..	2 – 4

Work carried out more recently at the Jet Propulsion Laboratory of the California Institute of Technology[10] has shown that almost complete recrystallization of beryllia can be achieved by firing for 2 hours at 2,000°C in an oxidizing atmosphere. The increase in grain size as a result of recrystallization was found to depend markedly on the initial particle size. The shrinkage caused by a 2 hr. firing treatment at 2,000°C. decreased about 17 per cent for a very fine beryllia (0 – 1.25) to about 5 per cent for coarser particles (20-30).

Beryllia is still a comparatively little-known oxide although its abundance in the earth's crust is almost equal to that of tin. In 1924 the world's output of beryl was about 10 tons, but in 1939 the consumption of the mineral by the U.S A. alone was about 500 tons.

Other Special Refractory Materials:—

Chrome magnesite may be looked on as the first successful attempt at "cross-breeding" in the refractories industry Many suggestions have been made for adopting the same procedure with the pure "thoroughbred" oxides, if the metaphor may be continued.

There is, in addition, an entirely new type of "cross-breed"; in this instance the breeder has not merely crossed two species, but has gone so far as to cross two genera — an achievement, it is thought, unprecedented in the animal kingdom. The result is the type of product variously called "metal-cermics," "ceramets" or "cermets"

Ceramets have resulted from the recognition of the fundamental similarity of the process of powder metallurgy and the sintering of ceramic oxides. Metal compacts have high strength and high thermal conductivity ; they can in consequence resist thermal hock ; on the other hand, they cannot be used at high temperatures Sintered oxides have exceptional heat resistance but are much more sensitive to sudden temperature changes In ceramets, an attempt has been made to produce a material that is resistant to spalling, is relatively light in weight and can be used at high temperatures Such a material would have great use in the production of gas turbines

IV. Refractory Materials as a Field for Research :

Various aspects of the subject of refractory materials as a field for research may be outlined as follows —

(1) Statistics and Publications
(2) Phase-Rule Investigations
(3) Physical, Chemical and Ceramic Properties of Raw Materials and Manufactured Products
(4) Standard Methods of Testing Refractory Materials.
(5) Raw material specifications and specification for Finished Products
(6) Manufacturing Methods.
(7) Coordination and International Cooperation.

(1) Statistics and Publications.

Although a classified bibliography of the extensive and widely-scattered literature on the subject of refractory materials and all matters relating thereto has been published, it is too old to be of much use and needs to be brought up to date and kept up to date by annual or periodic supplements

Bibliographic material may be supplemented by the preparation and publication from time to time of critical digests in the form of monographs on selected topics Each of these monographs should be an exhaustive critical presentation and discussion of all the essential known facts concerning the subject matter and should contain complete sets of tables of numerical data and a complete bibliography. Each important refractory material (silica, magnesite, kaolin, alumina, etc) might become the subject of such a monograph as might also the practice and requirements of each type of industry employing refractories. Not the least value of such a set of monographs would be its revelation of the relatively small amount of really reliable scientific data available on the subject of certain refractories and the enormous amount of work which still remains to be accomplished.

By cooperation of the appropriate governmental agencies such as the Bureau of Statistics and Census and the Department of the Indian Geological Survey, improvements in the collection of statistics relating to refractory raw materials and manufactured products can be brought about.

There is need for the more general diffusion of accurate information concerning the manufacture and use of refractory materials.

(2) Phase-Rule Investigations.

These are difficult and expensive scientific studies which are required in building up our scientific knowledge of refractory materials as chemical substances

As regards the common characteristic possessed by all refractory materials, that of resistance to high temperature, the initial problem presented for experimental investigation is to a large degree a problem in physical chemistry involving as its most important feature the application of the phase rule and the laws of solutions. Thus in accordance with the known laws of physical chemistry the effects of the presence

of impurities in a refractory material is always to decrease the refractory power, except when the proportion of the impurity is so large as to cause the composition of the mixture to coincide with a maximum point in the Phase-Rule diagram for the system, under which conditions the effect of the " impurity " may be either a decrease, an increase or no change at all in the refractory power depending upon the materials involved. According to the same laws, it is also in nearly all cases true that the larger the number of materials employed in the manufacture of a refractory product the lower will be its refractory power. Some of the patents issued for refractory materials cover products whose manufacture violates all the principles mentioned above. These principals are also violated in the rather widespread idea that as a general rule the refractory power of a given material can be increased by mixing with it a second more refractory material Some formulas given for calculating the refractory power (*i e.* softening point) of a mixture from its composition and the melting point of its components seem to have been formulated without regard to established physico-chemical laws.

Among the substances which may be included in the comprehensive phase-rule investigation of refractory materials are —

One component systems :—

$$ZrO_2 , BeO , ThO_2$$

Two or more component systems —

ZrO_2 , BeO , ThO_2 , C , SiO_2 , CaO , BaO , MgO , Al_2O_3 , Fe_2O_3 , Cr_2O_3 , Mo_2O_3 , TiO_2 , certain nitrides and carbides.

(3) Physical, Chemical and Technological Constants.

If a compilation is made of all the available data concerning the physical, chemical and ceramic properties of refractory materials and manufactured products, some accurate data will be found to be wanting especially for high temperature refractory oxides when subjected to different atmospheres and when heated under vacua.

The problem of crystal growth in ceramic bodies requires investigation. It is an important factor influencing the mechanical properties of ceramic bodies. Although crystallization from the glass phase is accompanied by a deterioration in mechanical properties and though

the larger the individual crystals which are formed, the more marked is the reduction in strength, yet magnesia is a material which is preheated before use in order to encourage crystals to develop. Some theoretical aspects requiring further elucidation in this connection are the mechanism by which crystal growth occurs and is promoted by certain mineralizers and the significance to be attached to the development of cleavage planes on subjecting periclase (MgO) crystals to a high temperature for long periods.

I would like to mention just one more problem here before passing on to the next section, that of inversion of high cristobalite to low cristobalite, these being the polymorphic forms of silica. This inversion is accompanied by an increase in volume amounting to 3 0 per cent and this is often detrimental to ceramic materials containing this mineral. If the high temperature form could be stabilized thus inhibing this inversion, it would mark a great advance in ceramic technology.

(4) Standard Methods for Testing Refractory Products.

The need for the development of standard methods for testing products in order that the results of such tests should indicate as clearly as possible the behaviour which might be expected of each material under service condition is obvious The methods to be employed in testing a given material would naturally vary according to the use to which the material was to be put. There is need for devising tests, which are, if possible, simpler than those existing and more suited to the requirements of Indian industries.

(5) Raw Material Specification, and Standard Specification for Finished Products.

Formulation of specifications to be met by each raw material employed in the manufacture of each type of refractory products is essential. These specifications would cover such factors as chemical and mineralogical composition, crystallographic condition, temperature, state of mechanical division, fusibility, and all the important ceramic properties such as plasticity, burning behaviour, properties developed upon burning, etc.

Among the largest users of refractory products, a list of which has already been given elsewhere, the drawing up of specifications which should be met by each type of refractory required in the corresponding industry is essential.

The subject is receiving the attention of the Indian Standards Institution, who have made a start by formulating specifications for fire clay refractories.

(6) Manufacturing Methods.

By the application of chemical engineering principles to the study of the processes employed in manufacturing each type of refractory, changes resulting in improvements in quality, decreased cost of production and increased definition and standardization of product, would be effected.

By the application of the same principles to the design and operation of industrial kilns and furnaces, with the object of establishing the best design of furnace or kiln and the most efficient method of operating the same for each particular industry or process employing high temperatures, many improvements can be effected

(7) Coordination and International Cooperation.

There are other aspects of the subject of refractory materials which require the cooperation of other departments, *e g*, in order to promote the extension of geological surveys (aiming at the location and mapping of deposits of refractory raw materials), to investigate any other geological problem of importance to the subject, and to secure the further development and the greater utilization of improved methods of mining, handling and preparing these materials, the cooperation of the Department of Mines and Geological Survey of India would be indispensable.

Similarly in arriving at the best designs for Industrial kilns and furnaces, the cooperation of the Fuel Research Institute will be desirable Likewise the services of the National Chemical, Physical and Metallurgical Laboratories and of the Indian Standards Institution will be of inestimable value to the National Glass and Silicate Research Laboratory and other regional laboratories like the Central Laboratories, Hyderabad in solving some of the research problems connected with refractories. Any desirable international cooperation in refractories research may also be undertaken if such a cooperation is in the national interest.

V. Some Specific Problems of Local and Regional Interest.

Having stated the various aspects of the subject of refractory materials as a field for research, I would like to mention here some of the

problems of local and regional interest on which work in the Central Laboratories, Hyderabad is either being done or will be done as soon as some of the problems on hand are completed The problems studied may be divided into two parts (*a*) The development of insulating refractory materials (*b*) The development of refractory materials

Satisfactory insulating brick can be produced from the following materials either by the chemical or mechanical process

(*a*) Local clays.

(*b*) Silica.

(*c*) Dolomite

(*d*) Kyanite.

By producing (refractory) insulating materials by mechanical means and incorporating a combustible substance such as powdered coal (coal fines), we shall incidentally be putting to good use a portion of our coal fines, the proper utilization of which is seriously engaging the attention of Dr. M S Iyengar and his associates in the Fuel Section of these Laboratories

Among the refractory products which could be developed, for which raw materials are available in the State, are

(1) *Semi-Silica Brick* Investigation on sand lime bricks have been completed in this laboratory. Some excellent semi-silica bricks can be produced from sand lime bricks by the process of heat treatment alone.

(2) *Silica Bricks* With abundant deposit of quartz of good quality and with the availability of sufficient quantities of coal, silica bricks can be produced not only to meet the local demand for such refractories but also to supply the demand of a good portion of South India as well

Mr B S R Sastry will be taking up this problem as well as the problem of production of semi-silica bricks in due course, and will be making a study of the mechanism of polymorphic transformation of silica.

(3) *Refractory bricks from local clays* Dr K. Venkateswar Rao of the Mines and Geological Department, Hyderabad as well as Mr. Balbhim Rao of the Central Laboratories have conducted investigations on the

different properties of Hyderabad clays ; this should be very useful in determining the suitability of our clays for the manufacture of refractories as well as for different ceramic and allied industries. Mr. M.D. Narasimhan is making a detailed study of the problem of making suitable fire clay refractories from local clays.

(4) *Development of graphite crucibles from local graphite.*

(5) *Development of silicon carbide.*—The problem could only be undertaken when cheap electricity is made available by the completion of the hydroelectric scheme at Tungabhadra.

VI. Conclusion.

The refractories industry is a basic industry, whose products are used by such other important industries as iron and steel, various non-ferrous metals industries, the gas industry, the by-product coke industry, the glass industry, the pottery and porcelain industry, the brick, tile and sewer pipe industries, the cement industry, the various industries employing electric furnaces, the enamelling industry, the great variety of chemical industries employing high temperatures and the power plants of the country.

This industry is of national importance being indispensable in peace and war. In America refractories were placed along with iron and steel among the ten most important materials for the production of war essentials. The conservation of coal and other fuel resources of the country is intimately linked up with the production of improved type of refractories and of insulating materials. Considering the above facts, I hope the National Planning Committee will in their deliberations give the subject of refractories the consideration it deserves and not only provide sufficient funds with which to stimulate research on the development of special refractories, such as zircon, beryllia, some rare earths and others, for which the raw materials are found in the country, but to the same end will bring about coordination between different National and Regional Laboratories of the country.

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DISCUSSION

Participants :

1. Dr. H. G. Kayser. Laxminarayana Institute of Technology, Nagpur. (*Chairman*)
2. Dr. M. S. Iyengar, Central Laboratories for Scientific and Industrial Research, Hyderabad-Dn.
3. Dr. S. Z. Ali, –do–
4. Mr. Abde Ali, Department of Applied Chemistry, Osmania University, Hyderabad-Deccan.
5. Dr. M. G. Krishna, Central Laboratories for Scientific and Industrial Research, Hyderabad-Dn.
6. Mr. B. S. R. Sastry, –do–
7. Mr. M. D. Narasimhan, –do–

The importance of refractories, the close relation of refractories to fuels which are burnt in refractory containers, and the *need of research on refractory materials* was stressed (H G K.). The *necessity of conservation of fuel* by thermal insulation of acidic, basic, and neutral refractories

was evident from the fact that about 30-50 per cent of the heat supplied to a furnace was lost by radiation. With proper insulation an appreciable amount of this heat loss could be avoided (M. D. N.).

The *mechanism by which certain impurities* and other factors, such as a reducing atmosphere, *foster crystal growth* was brought under discussion Although in general crystallisation from the glass phase is accompanied by a deterioration in mechanical properties and the larger the individual crystal, the more marked is the reduction in strength, yet magnesia is a refractory which is preheated before use in order to encourage large crystals to develop The beneficial effect of iron oxide in increasing the crystal size was attributed to the formation of magnesium ferrate which is soluble in periclase crystals at a high temperature (M D N) However, it was contended (A A) that theories based on solution effects promoting crystal growth cannot be used to explain the mineralizing effect of silica and lime, which have a more pronounced effect on dead burning of magnesite than iron oxide, as it is unlikely that these oxides (SiO_2, CaO) form minerals which are soluble to any extent in periclase crystals The enhancing of crystal growth in a reducing atmosphere could be explained by any theory which posulated the partial dissociation of magnesioferrate to FeO followed by its reformation on cooling (when an oxidising atmosphere prevailed) It is probable that measurement of oxygen pressure in the MgO-FeO-FeO_3 system would provide confirmatory data on this subject.

Information was sought regarding *the use of X-rays in the study of the action of FeO on MgO* (S.Z A.). It was stated (A.A.) that little work had been done on the subject and the known facts were that magnesioferrate and periclase both crystallize in the cubic system , the cell size of MgO is only half that of the spinel (magnesioferrate)

An opinion was expressed that *stabilization in silica brick* cannot be effected by the addition of lime, as 5-7 per cent lime decreased the refractory properties of a silica brick by 200-300°C. (M D N). Lime which successfully stabilizes zircon need not be used as a stabilizing agent for silica brick. There was a great need for investigation for a desirable substance which should stabilize silica and modify its expansion and consequently the spalling resistance of silica brick If a substance could be found which could inhibit high cristobalite inversion to low cristobalite, the change being accompanied by an increase in volume

to the extent of 3.0 per cent which is often detrimental to these materials, it would mark a great advance in ceramic technology (A A.).

A question was asked regarding *the comparison of zirconia and zircon refractories and the influence of the presence of impurities on zircon* (M S.I). Zirconia refractories, it was pointed out (A.A.), withstand higher temperatures than zircon bricks. The latter by reason of their ability to dissociate to give silica should be classified as acid rather than as neutral refractories. Zircon resists coal ash slag well, and has lower thermal expansion, higher thermal conductivity and greater volume stability than zirconia bricks As regards the effect of impurities on zircon they in common with the reducing atmosphere of the furnace tend to lower the dissociation temperature, the products of dissociation esxpanding and tending to shatter the crystals of zircon Some interesting microphotographs of zircon, showing the cleavage of crystals, were shown (M.S.I.).

As the acid-resistant enamels were poor conductors of heat and the alloys, which had good thermal conductivity, were poor in acid resistance, was it possible by some cross breeding methods mentioned *to produce a material with good acid resistance and at the same time good heat transfer* (M G.K.) ? A view was expressed (H.G.K.) that there was a basic difference between enamels and refractories Enamels should not be porous and refractories should be porous to withstand sudden temperature changes. It was not possible to have heat transfer and acid resistance combined in the same material Another view was expressed (B.S.R.S) that as the oxides used in enamels are inherently poor conductors and metals good conductors, a compromise could be effected by the use of a minimum thin coating of enamel which would improve the heat transfer. " Cermets," products resulting from the cross-breeding of metal and ceramic products (A.A.) held out a possibility of supplying a material having both the desirable properties of good acid resistance and good heat transfer.

An opinion was expressed that the *expression* $R = \frac{M}{\Delta E}\sqrt{\frac{K}{dc}}$ which was given *for calculating the resistance to spalling* of a brick was inadequate and dimensionally unbalanced (H.G.K.). It was pointed out (A.A.) that M, which was the strength factor in the expression had two different values depending upon whether the material was being subjected to tensile stresses or compressive stresses.

A SURVEY OF X-RAY ANALYSES OF COALS

by

DR. (MISS) S. Z. ALI

(*Central Laboratories, Hyderabad-Deccan*)

1. Origin of Coal:-

Coal has been formed from vegetation which grew a long time ago when the surface of the earth was slowly undulating Large masses of land with the accumulated vegetable debris slowly subsided to become, in many cases, marine basins or deltaic areas where sedimentation occurred. This in turn resulted in the eventual silting up of the depression and, together with the uplifting of the earth's surface, led to the reformation of a land area and another period of vegetable growth. Although we are still very much in the dark as regards the exact chemical constitution of the resultant coaly matter, the broad facts regarding the nature of the processes that led to the conversion of the vegetable debris into peat, brown coals and lignites, bituminous coals and into anthracite have been established Apart from the above-cited series in which coalification occurs, a typical lump of banded bituminous coal, taken from a coal seam, generally shows four different constituents These have been distinguished by Stopes (1) as 'durain' for the dull coal, 'vitrain' for the glossy coal, 'clarain' for the silky coal and 'fusain' for the mineral charcoal Vitrain is generally regarded as the fundamental coal substance.

2. Radiographic studies of Coal :—

The discovery of X-rays in 1895 placed in the hands of scientists a powerful tool with which the intrinsic arrangement of atoms in solids, liquids and gases could be successfully investigated, and coal being a very useful substance to man has been studied in its various forms. Though the last word regarding the structure of coal has not been said, much work has already been done and it would be useful to try to give an outline of the work so far done.

The first radiographic examinations of coal were made at the Mines Hospital near Saarbrucken in 1897. C. Norman Kemp (2) during

the first two decades of the century systematically used the technique of radiography for the study of coal. As the X-ray photograph gives a denser positive image for ash and extraneous matter than for coal, it is quite feasible to determine the relative proportions by volume of coal and non-coaly matter. The quantitative estimation of the distribution of refuse by weight is a complicated matter where the chemical constitution of the refuse has to be taken into consideration. The minerals associated with coal are not all equally impervious to X-radiation whose absorption depends on the atomic number of the element, *i.e*, for a given X-wave length, the mass absorption co-efficient, *viz.*, the fractional decrease in intensity for a beam of unit cross section per unit mass of material, is far greater for an absorbing substance of high atomic number than for one of low atomic number.

Fluorescent screens or photographic films may be used to register the partially absorbed X-ray beam after it has passed through a suitably thick section of a coal sample, normal or parallel to the bedding. The radiographic method has been utilized in the laboratory to judge the effectiveness of the jigging operation (3) and for rapid determination of the efficiency of coke—and coal—cleaning processes (4). It has also been found that whereas the coal substance is comparatively translucent, durain appears more opaque than its ash content warrants. A number of Indian coals from the Jharia coalfield have been studied by the radiographic method by Forrester (5). Washability tests were carried out by him on 23 samples from various seams and X-ray photographs of 24 samples of the coal of the field were prepared. These tests along with the evidence of the X-ray examination showed that only small reductions in the ash content of the coal samples of about 2 inches in size could be expected by the application of the normal washing processes, while on the other hand smaller sizes of screened Indian coals might respond to these processes. It is quite feasible to study the nature of porosity in coals by taking radiographs of coal slices soaked in aqueous solutions of lead salts It was found by Beeching (6) that dull coals were penetrated by the solutions, but bright coals were not, and fusain was usually more porous than durain.

Coal has been stereo-radiographically studied by Kemp and also by Wilson (7), who has described the procedure in detail and has discussed the use of stereo-radiographs to indicate the probable manner of fracture of coal due to subsequent mechanical handling.

3. X-ray diffraction studies of Coal :—

X-ray diffraction methods depend upon the fact that when a collimated beam of X-rays (monochromatised in the case of powder and single crystal rotation methods) is directed on the specimen, the reflected radiation diverges at various angles which are characteristic of the crystal structure. The specimen may be in a finely divided form when it will give the characteristic powder pattern on a photographic film, or it may be a small single crystal which will give its own characteristic pattern If the finely divided substance is crystalline, that is, there is order in its atomic arrangment, the powder lines are usually uniform concentric rings, but if there is a high degree of disorder or if the powder is colloidal, the pattern consists of a number of broad, diffuse halos, and is often more difficult to interpret than that of a crystalline substance. Carbon in the form of diamond is a very well-known crystalline substance. Graphite is also crystalline (8), consisting of a series of parallel planes of carbon atoms at an equidistant spacing of 3 35 A, each plane containing carbon atoms grouped in a hexagonal lattice arrangement. Further work by Bernal (9) and by Lipson and Stokes (10) has elucidated the structure of graphite in greater detail. The X-ray diffraction patterns of coals and the so-called amorphous carbons show a few diffuse bands, which, however, nearly correspond in position with the sharper lines of the graphite pattern and it was early postulated by Debye and Scherrer that all ' amorphous ' carbons were degenerate forms of graphite As a result of X-ray studies over the past two decades, it is known that as crystal size gets smaller there is a limiting average of about 10^{-4} cm , below which the powder lines show diffuseness and in fact become broad halos on further decrease of particle size. In coal, the state of disorder of the crystallites as well as their size is responsible for the diffuse halos which are obtained even without powdering, by just putting a flat photographic plate behind the specimen.

Mahadevan (9) was one of the first users of X-ray diffraction methods for the study of coal, working on both vitrain and durain sections and on solvent extracts. His samples of vitrain, which he regarded as of homogeneous composition and structure, exhibited two diffuse halos which correspond to the two most prominent rings of graphitic carbon. He also observed that the scattering between the two halos appeared to be related to the sum of the moisture content and volatile matter content. Mahadevan noted that the superpo sition of ash and

graphite halos on a vitrain pattern gave a durain pattern. Corriez (10), in examining peranthracites and true anthracites, confirmed the similarity of the anthracite structure to the graphite lattice and concluded that the mean distance between the layers of carbon atoms of both types of anthracite is of the order of 3 6 A, with a small but constant number of such lattices making up the crystallite.

The effect of heat on carbon has been studied by X-ray methods by H. L Riley and his co-workers (11, 12), who made a thorough investigation in this field. They studied the carbonisation of coal and naturally occurring coals and other combustible materials over the usual temperature range of carbonisation Up to 700°C, the crystallites, according to them, appear to grow by lateral extension of the layer planes without significant growth in the plane normal to this, *i e*, the number of carbon hexagons in rigid linkage grows by elimination of volatile matter attached to the free ends of the carbon atoms. Above this temperature this growth slows down while no appreciable growth occurs in the normal plane until the temperature rises above 1200°C. when the number of layer planes increases and growth continues also in the layer planes as shown by the fact that the diffuse lines on the X-ray pattern begin to sharpen appreciably The studies of the X-ray powder lines, becoming sharp at elevated temperatures, throw considerable light on the process of coalification occurring in nature. From the carbonisation studies carried out by the above workers it is evident that both carbonisation and coalification are processes which involve 'aromatisation' of the carbon atoms

The X-ray diffraction studies of various coals show interesting features as the rank or carbon content increases, starting from peat to anthracite. Riley and his co-workers have estimated the crystallite dimensions using the intensities of the 002 and 100 'reflections.' As it was possible to obtain only two dimensions, the assumption (13) they made was " that the carbon crystallites consist of small cylinders, the average height (c dimension) of which is determined from the 002 band, and the average diameter (a dimension) of which is determined from the 100 band. This gives, of course, only an approximate average picture of the state of affairs obtaining . the X-ray photograph gives no information as to the state of aggregation of the crystallites."

Table I gives a summary of their results, obtained for the coals studied upto 1943. It is seen that the size of the crystallite increases as the rank increases from peat to anthracite.

TABLE I

ANALYSES AND CRYSTALLITE DIMENSIONS OF COALS OF VARIOUS RANK

[from Riley *et al.* (11, 12)]

No.	Sample No.	Description	Analysis a. f. d. %		Crystallite Dimension A	
			C	H	a	c
1	C. 427	Irish Peat . .	56 59	5.34	17 7	10 4
2	—	Dopplerite . . .	56 68	4 76	19 4	11 8
3	C 445	Irish Peat .	57 22	5 27	18 7	10 1
4	C. 458	Polish Brown Coal	68 18	5 36	19 7	12 1
5	C. 457	Polish Lignite	69 70	4 24	19 4	12 6
6	—	Whitby Jet .	79.30	5 53	19.7	11 1
7	C. 642	West Yorkshire Coal	80.85	5 23	20 9	12 9
8	C. 698	Northumberland Coal	81 70	5 19	19 9	13 3
9	C. 695	Northumberland Coal	82 07	4 83	20 2	13.4
10	—	Backworth Cinder Coal	84 84	5 09	20 9	13 9
11	C. 608	South Wales Coal .	86 20	5 37	20 7	14 3
12	C 599	Busty Vitrain	87 00	5 03	20 5	16 2
13	C. 383	Durham Coal .	88.36	4 81	20 7	14 5
14	C. 609	South Wales Coal .	89 00	5 15	20 6	14 9
15	C. 610	South Wales Coal .	89.40	4 91	20.6	15 1
16	C. 611	South Wales Coal	90.60	4.67	21 0	15 4
17	C. 601	Busty Fusain	91 46	3 20	25 9	12 3
18	C. 612	South Wales Coal	91.60	4.43	21.6	16 2
19	C. 613	South Wales Anthracite	92 30	3.97	23 0	17 1
20	C. 607	South Wales Anthracite .	92 50	3 37	23 7	17.2
21	C. 620	American Anthracite	93.06	2 92	24 2	17.5
22	C. 527	South Wales Anthracite	93.64	2.75	26 6	16.4
23	C. 544	South Wales Anthracite . .	93 90	3 50	23 9	17.0
24	C. 784	Scottish Anthracite .	94 46	1 28	32.9	14 7
25	C. 617	American Anthracite .	94 93	2 05	27 5	15 8
26	—	Brockwell Fusain .	95.10	2.50	29 4	12.2
27	C. 618	American Anthracite . .	95 90	1.93	30.1	13.8

D. P. Riley (15) has reported work on the low-angle scattering of X-rays by various coals as distinct from the line-broadening studies of the X-ray powder pattern mentioned above. Crystals give a very small background scattering at all angles to the incident beam, the X-rays being diffracted almost entirely in the near neighbourhood of the Bragg-reflection directions, while liquids give a diffuse ring, inside which the scattering decreases continuously as the diffraction angle diminishes The scattering of X-rays at small angles to the incident beam is very small for crystals because of the structural regularity and close packing of the constituent particles , it is small for liquids also But for some, the so-called amorphous solids, the low-angle scattering is considerable, being quite distinct from a diffuse ring or halo, in that the diffuse blackening round the central spot on the film does not diminish appreciably as the central spot is reached as in the case of a halo. This low-angle scattering is often more intense that the rest of the film and for some forms of carbon black, it is the most characteristic feature of the diffraction pattern.

Low-angle scattering of X-rays arises from the fact that the specimen subjected to X-rays, consists of very small particles or groups of particles, arranged at random This scattering is independent of the internal atomic structure of the individual particles, which may be crystalline or amorphous, and is related solely to the size, shape and mutual arrangement of the particles themselves, whereas the boardening of X-ray powder pattern lines is related to the size of the *crystallites* comprising the powder, and to disordered structure, if present, in the crystallites themselves. Very refined experimental technique is required in the study and interpretation of the low-angle scattering from 'amorphous' solids, when crystal-reflected, strictly monochromatic radiation has to be employed for obtaining the scattering pattern which again has to be interpreted with the help of Fourier methods applied to the full intensity curve. In line-broadening studies also, monochromatic and carefully collimated radiation has to be employed and in the interpretation of the intensity curve obtained, the worker has to determine very carefully which of the two main factors, *viz.*, crystallite size and disorder is more likely to be effective in producing the line-broadening obtained or whether both factors are effective. Further work on these lines has to be done before the 'approximate' and 'statistical' picture of the coal structure as obtained by H. L. Riley

and others can be made more exact (cf. The Ultrafine Structure of Coals and Cokes, 1943, p. 213, section 6).

X-ray diffiaction studies have been made for the identification of non-coal minerals in coal by Nagelschmidt and Hicks (16). The most common minerals in coal are clay minerals, the three most common groups of these being the kaolin, hydrated mica and montmorillonite groups, carbonates and sulphides. Kaolinite has the structural formula $Al_2 Si_2 O_5 (OH)_4$ and mica, $K Al_2(Al Si_3)O_{10} (OH)_2$. The hydrated mica in clays contains usually less potash, more silica and more water. Most clay minerals have layer structures, the silicon-oxygen tetrahedra forming the basic, hexagonal network or sheet with the hydroxyls and the cations occupying positions with reference to a single sheet as in the kaolin group, or in between two sheets, one inverted over the other, as in the hydrated mica and the montmorillionate groups whose structures are closely related For quantitative determinations of mixtures of clay minerals it is usually necessary to combine X-ray analysis with chemical, dehydration, base exchange and similar studies. The carbonates and sulphides can be indentified by their characteristic powder lines, but for clay mineral identification, careful elimination of possible clays has to be done. Nagelschmidt and Hicks (*loc. cit.*) found that the roofs and clods of certain Welsh coal mines consisted mainly of hydrated mica, termed " illite " by American workers, and quartz in varying proportions with small amounts of kaolin and carbonates, but the mineral matter in the lightest coal fractions was very similar from one sample to another, its chief constituent being kaolin The minerals kaolinite and halloysite both belong to the kaolin group but halloysite has a lower degree of ordered structure than kaolinite The mineral matter in some of the anthracite samples was closer to the halloysite type and that of the bituminous samples, more closely related to the kaolinite type, but further work is required to establish the conclusion. The mineral matter of the heaviest coal fractions was complex and varied from sample to sample. All contained large amounts of carbonates, chiefly siderite $Fe CO_3$, or ankerite $(Ca, Mg, Fe) CO_3$—dolomite $(Ca, Mg) CO_3$, while calcite $Ca CO_3$ was comparatively rare.

The interesting problem of the ordering of the coal substance by the presence of fine sheets of mica and kaolin-type minerals, found in the well-marked " bright " and " dull " striations of a Welsh coking-coal has been investigated by D. P. Riley (17).

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DISCUSSION

Participants :

Dr H. G. Kayser, Laxminarayana Institute of Technology, Nagpur. (Chairman).

Dr. S. Husain Zaheer, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn.).

Dr. Sultana Z. Ali, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn.).

Dr. M. S. Iyengar, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn.).

Dr. S. A Saletore, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn).

Mr. R. J. Sujir, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn.)

Mr. J. Lakshmikantam, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn).

Mr S S. Ghosh, Indian Institute of Science, Bangalore

Dr N S Rao, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn).

A question was asked (S H Z) as to whether the electron microscope could be used to determine the structure of coals In reply it was stated by the main speaker (S Z A.) that the electron microscope could be useful in finding the shape and size of the coal particles provided the thickness of the specimen was carefully controlled. It was stated (R.J.S.) that the electron micrograph of a coal specimen showed a hexagonal shape and the specimen had to be very accurately machined to about one μ thickness

Discussion then centred on the *de-aromatization of coals* One of the speakers (N S R.) felt that as aromatization was possible with increase in temperature, the reverse process, namely the de-aromatization of coal should be possible with lowering the temperature to, say, liquid helium temperature, and probably an easy method of manufacturing benzene should then be possible. However it was felt (S.S.G.) that since aromatization was a stable, thermal phenomena during which the coal decomposed and the volatiles escaped, the reverse process was not possible. Further it was stated (M S I) that coal substance comprised a number of hexagonally arranged carbon atoms to some of which the volatile radicals were attached Upon heating the coal the volatile radicals were eliminated. The question was raised (S.A.S.) that if the coal substance contained carboxyl groups attached to the hexagonal frame-work then coal should react with an alkali to give soap. In reply it was stated (M.S.I.) that coal reacts with an alkali and has a saponification value. It was further stated (H.G.K.) that the iodine value of coke increased with temperature up to a point; with further increase in temperature the value decreased.

Was it possible by *X-ray methods* to determine quantitatively the *amount of sulphur* present in coal (J L)? In reply it was stated by the main speaker (S.Z.A) that theoretically it was possible to estimate sulphur in the form of various sulphides by X-ray methods , since easier chemical methods were available for estimation of sulphur in coals, X-ray methods may not be used in practice for sulphur determinations (M.S.I.).

Discussion then centred round the question (J.L.) whether X-ray methods could be employed for *estimation of ash in coals* The main speaker (S Z A) felt that quantitative estimation of ash and its nature could be made by X-ray radiographs and diffraction studies provided preliminary data from survey as regards the chemical nature of the non-coaly matter was available and provided a correlation between the chemical analyses and the X-ray diagrams were established for the homogeneous representative seams in the coal-field X-ray diffraction photographs showed the minerals present in coals apart from indicating *the state of coal* itself, whereas X-ray radiographs showed the distribution of non-coaly substance in a sample of coal Further it was stated (H G K.) that during the last war in Germany stereo-radiographic methods had been used to find the distribution of intrinsic ash in brown coals and in briquettes prepared from them, before carbonisation and after carbonisation A point was raised (S S G) that whereas by chemical analysis of Jharia coals it was found that they belonged to the bituminous group, the X-ray analysis method placed them in the sub-bituminous group It was pointed out (M S I) that with the somewhat insufficient data available on Indian coals and without systematic analyses of all coals, any attempt to classify coals from data available on unrepresentative samples would lead to erroneous conclusions.

The importance of X-ray methods of investigations *for predicting the coking properties of coal* as established by Prof. Riley was emphasised in conclusion (H.G.K.).

MODERN CONCEPTION OF FLAMES

by

Dr. M. S. Iyengar

ntral Laboratories for Scientific & Industrial Research, Hyderabad-Deccan)

The development of the phenomena of combustion and ' slow nbustion ' are briefly described. The influence of factors e ' flash back ' and ' blow-off,' on the stability of diffusion mes and pre-mixed flames are discussed. Recent theories garding the propagation of flames and the role that hydrogen oms and radicals play in carbon deposit formation in flames e presented.

roduction

The energy needed for almost every industrial operation is pro-ed by flames directly or indirectly. An understanding of the mecha-m of flames is therefore of vital importance. Unfortunately this chanism is not yet completely understood. A number of papers ve been published in recent years on different aspects of flames. In s paper an attempt is made to bring together all the known facts garding flames and to link them up with the work that is being pur-d in our laboratories on combustion and carbon deposit formation flames.

On sparking a sample of the mixture $2CO + O_2$ alone, Dixon in 77 found that such a mixture, previously kept in contact with solid assium hydroxide, would not ignite[1], but when a small quantity of ter vapour was added the mixture at once became explosive Dixon, colloboration with Baker, showed that hydrogen and various hydro-n-containing compounds, *e.g.*, ammonia or methane, could also der a dry mixture potentially explosive. The experimental obser-ion of Dixon, considered in the light of the mass law and the kinetic ory, proved a stumbling block to the chemists of the last century. was left to Bone[2,3], continuing Dixon's researches, to demonstrate tween 1926 and 1929 that the dry gases carbon monoxide and oxygen l combine provided the igniting source is sufficiently powerful. This

was followed by the work of Weston[4], Garner[5] and others which established the existence of both a ' wet ' and a dry ' reaction.

Until about 1925 the ' thermal ' view held the field, according to which rate of reaction depended upon temperature alone ; when the latter was raised, the rate of reaction increased until a point was reached at which the rate of heat release to the system exceeded that of its dissipation, the reaction becoming autogenous with the initiation of flame. A number of observations, many of which came to light about that time, led to the overthrow of this simple view and its replacement by the theory of chain reactions. About 1930, Sagulin[6], Hinshelwood[7], Garner and Gomm[8] and Semenoff[9], established the existence of lower and upper limits of pressures at which explosion occurs in an explosive mixture. The existence of an explosive region is inexplicable on the basis of a purely thermal concept of explosion Other typical observations which led to the overthrow of the ' thermal ' view were .

a. the dominating part played by materials in small concentration, *i.e.*, inhibitors and promoters ;

b. the occurrence of long induction periods, sometimes hours, before reaction set in and spontaneous ignition ensued ; and

c. the part played by inert gases in not retarding reaction but actually accelerating it.

The ' chain ' view shows how reaction is not dependent upon temperature rise alone, but upon the fact that the energy released is confined to specific molecules or molecular fragments, mainly atoms and radicals, and that it is passed on from one molecule or fragment to the other, the overall reaction rate being determined by branching or multiplying, and breaking or destructive processes. The reaction between carbon monoxide/oxygen and oxygen/hydrogen which are similar in many ways are represented in the following as a chain reaction :

H_2/O_2	Moist CO/O
Chain initiation	
$H_2+M \longrightarrow 2H + M$	$CO + H_2O \longrightarrow CO_2+H_2$
	$H_2 + M \longrightarrow 2H + M$

Chain propagation

$$OH + H_2 \longrightarrow H_2O + H \qquad OH + CO \longrightarrow CO_2 + H$$
$$HO_2 + H_2 \longrightarrow H_2O + OH \qquad HO_2 + CO \longrightarrow CO_2 + OH$$

Chain branching (identical)

$$H + O_2 \longrightarrow HO + O$$
$$O + H_2 \longrightarrow OH + H$$

Flames

By flames we generally mean a rapid chemical change occurring in a thin layer of explosive mixture accompanied by luminosity. There are two types of flames. One is a diffusion flame as typified by a candle flame. Here the fuel vapour rises from the wick and burns in its neighbourhood to the extent that it is mixed with oxygen of air either by turbulence or diffusion. The other type of flame is called a pre-mixed, aerated or explosive flame. Here we have the explosive mixture present from the very outset. Both these types of flames are typified by the dual character of the Bunsen flame. The inner cone of the latter is an explosion flame, the rate of flame-travel being compensated by the feed velocity, thus rendering it apparently stationary; the outer cone is a diffusion flame where combustion depends, *inter alia*, upon the relative diffusion rates outwards of the combustible constituents and inwards of the oxygen of the atmosphere.

FACTORS INFLUENCING THE STABILITY OF DIFFUSION FLAMES

(*i*) *Flame Flicker*

The phenomena of flicker in diffusion flames is closely related to the flow conditions prevailing in the gas stream. A flame apparently starts to flicker when the apex of the turbulent section of the stream enters within the zone of active combustion, or, in other words, when the height to turbulence in the burning gas stream becomes equal to or slightly less than the height of the flame. In this connection it should be borne in mind that the height to turbulence in a burning stream is greater than that in an unignited stream at the same rate of flow because of the temperature effect[10].

(*ii*) *Flame Lift*

Precise information on flame lifts is lacking, but it is obviously associated with that portion of the flame adjacent to the jet orifice. The transition to turbulence within the gas stream has apparently no direct effect upon lift for, in certain instances, as with very fine orifices, a flame may lift before it flickers, showing that the gas flow had remained laminar along the entire length of the flame The phenomena may be explained in terms of diffusion velocity distribution, or even on thermal grounds, but it seems likely that, with increasing efflux velocity, the ring which forms the base of a diffusion flame, and which at low gas flows is of considerably greater diameter than, and may even be situated below, the jet orifice, moves progressively upwards and inwards until it reaches a position where the gas velocity exceeds the burning velocity, when it moves downstream

(*iii*) *Flame Blow-off*

The phenomena of blow-off is peculiar to diffusion flames. The experimental investigation of blow-off is a difficult one for it involves measuring the velocity of the gas from point to point in the stream, and the stream normally used is so small that the use of any device such as a pitot tube is bound to alter the flow pattern Moreover, flow in the air surrounding the jet is a very important factor, but the velocity is so much lower in the jet that greater care must be taken to avoid drafts and special technique must be evolved for measuring it. The Gas Research Board at the University of Leeds has been investigating this particular problem and has been able to suggest a reason for the blow-off The new theory suggested by them is that the combustion at the base of the flame is smothered by products of combustion carried thither presumably by the eddying currents in a vortex ring round the mouth of the orifice Scholefield and Garside[10] have been able to show that lifting of flames can take place without there being any change from stream line to turbulence and that velocity distribution alone will not account for it. They also showed that lifting of the flame could be artificially stimulated by adding combustion products to the base of flame. In Figure I (*see page* 88) (obtained by Scholefield and Garside) the stability ranges of diffusion flames on carburettor-type jets are shown.

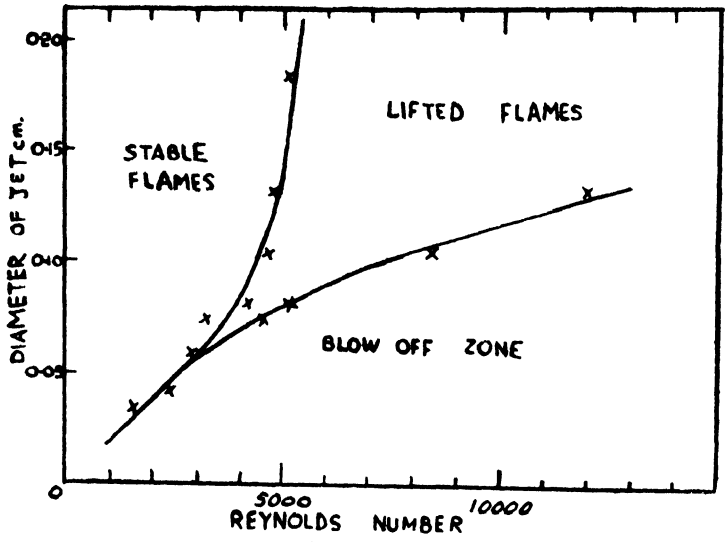

Fig. 1

FACTORS INFLUENCING THE STABILITY OF PRE-MIXED FLAMES

Lewis and von Elbe[11] have enlarged upon the effect of low burning velocity at the edge of the inner cone upon flame stability and have advanced a theory to explain both the light-back and blow-off of aerated flames in terms of a so-called velocity gradient at the boundary of the gas stream Figures 2a and 2b illustrate, respectively, conditions for light-back and blow-off. The thick line in Figure 2a represents the variations in burning velocity over the inner cone from its base inwards towards the burner axis. The three thin lines represent various velocity profiles of the unburnt mixture. It is propounded that light-back will occur if the burning velocity exceeds the gas velocity anywhere in the stream, as indicated by line I ; that, at a somewhat greater flow, a critical gradient of the gas velocity at the stream boundary will be reached, as shown by line 2, where light-back is just possible ; and that, at flows in excess of this critical value (line 3), the flame will be stable until blow-off occurs.

The conditions visualized for blow-off are shown in figure 2b. The flame is assumed to establish itself at some distance above the burner port, when the conditions are as represented by the lower of

the two thick lines and thin line 1, *i.e.*, at some point in the stream the burning velocity equals the feed velocity. As the mixture flow is increased it is postulated that " the combustion zone moves away from the rim and thus gains in burning velocity until a new point of equality is established farther out and farther above the rim," a set of conditions illustrated by the upper thick line of Figure 2b The combustion zone, however, cannot continue indefinitely to accomodate itself to progressive increases in gas flow ; eventually the gas velocity everywhere exceeds the burning velocity (thin line 3), and the flame is unstable At

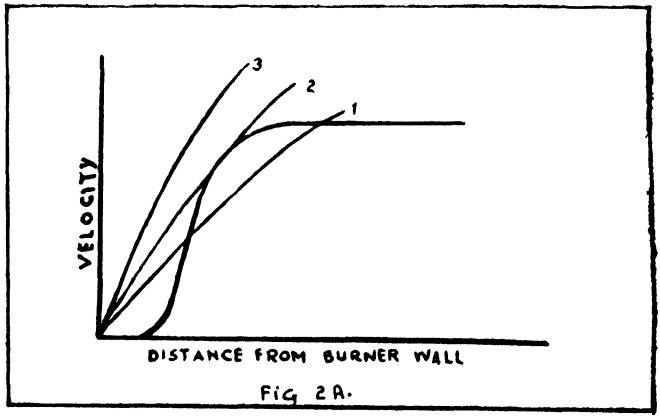

FIG 2A.

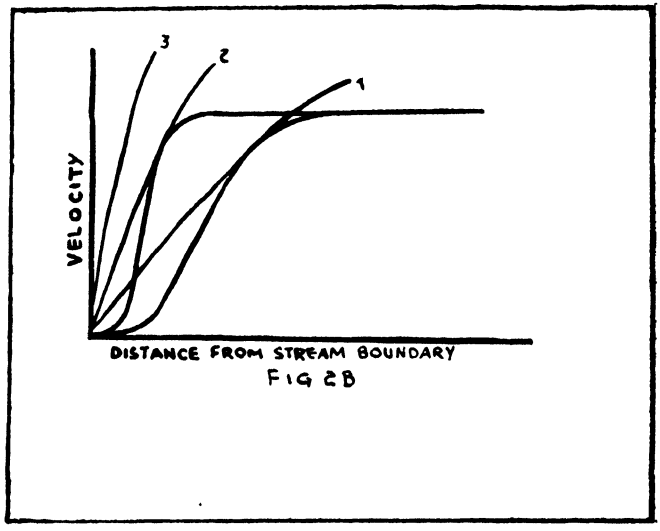

FIG 2B

some slightly lower flow (thin line 2), a critical velocity gradient is reached at which the flame just blows off.

The recent work of Forsyth and Garside[12] seems to indicate that the most important factor affecting flash-back in aerated burners is the 'dead space' Dead space has been interpreted as a thermal gradient ahead of the flame In the case of ethylene-air mixtures, the flash-back limits have been found to vary materially with pressure, although there is hardly any corresponding change in burning velocity On the other hand, the variation of flash-back limits with pressure have been shown to follow closely that of dead space with pressure for each mixture In the light of the above considerations Forsyth and Garside have explained the phenomena of flash-back as follows Under conditions of laminar flow the velocity of the gas-air mixture is distributed across the burner section according to a parabolic profile, the velocities near the burner wall being low and those along the burner axis a maximum Owing to its thermal gradient, a flame cannot approach the burner wall nearer than a distance equivalent to the dead space, hence the feed velocity to be overcome by the burning velocity is not the average velocity but that at the dead space distance from the burner wall In general, flash-back is proportional to the ratio of burning velocity to dead space.

IGNITION VELOCITY OR FLAME SPEED

Heiligenstaedt[13] has defined ignition velocity as the volumetric rate of flow of combustible mixture through unit area of the inner cone surface There are two methods of measuring flame speed. One is the burner method and the other the soap bubble method In the burner method the shape of the bunsen cone is determined when premixed gases are being burnt The flame speed is determined either by dividing the area of flame cone by the volume of gas flow or by determining the gas flow rate, resolved normally to the flame surface at the various parts of the cone If A_R is the angle the gas flow line makes with flame surface at a radius R, and the gas flow rate is V_R, the flame velocity is given by V_R. Sin A_R In employing this method, most of the workers have used the visible cone Linnett and others[14] in recent years have preferred to use the shadow cones obtained when light from an external source is passed through the flame and a shadow is cast on a surface beyond the flame.

In the soap bubble method, developed by Linnett[14], a soap-bubble is blown with the explosive gas mixture A spark gap is pushed into the centre of the bubble and the mixture is sparked. This causes the mixture to explode The central horizontal strip of the bubble is photographed on a rotating drum camera Successive portions of the film are exposed at successive moments of time Therefore distance across the film represents distance across the middle of the bubble and distance along the film represents intervals of time

PROPAGATION OF FLAMES

The view of flame propagation originally propounded by Le Chatelier in 1881 was that unburnt gases ahead of the flame front were raised to the ignition temperature by the conduction of heat from the burning zone. This view no longer seems to hold true in the light of recent growing belief that atoms are present in flames in concentrations exceeding those predicted on the basis of thermo-dynamic equilibria involving atoms, *e.g* $H_2O \rightleftharpoons OH + H$, $CO + OH \rightleftharpoons CO_2 + H$ There have been two outstanding examples of experimental evidence for the presence of such atoms Smith[15] has demonstrated that the beautifully coloured luminescent effects produced by contact of the flames of hydrogen-containing gases with calcium oxide surfaces promoted by the oxides of certain metals, *e g* antimony, pink , magnesium, golden yellow , and bismuth, violet, were the outcome of the energy liberated by the recombination of hydrogen atoms on their surfaces Dooley and Whittingham[16] have demonstrated that the sulphates and sulphuric acid responsible for deposits and corrosion, respectively, in water-tube boilers are the outcome of the combination of oxygen atoms and sulphur dioxide liberated from the fuel bed Tanford and Pease[17] have shown that in flames where carbon monoxide or hydrogen are present there exists a relation between experimental burning velocities and the hydrogen atom concentrations in the burnt gases. On this basis they have suggested that diffusion plays an important role in the combustion process, presumably by maintaining a high, non-equilibrium concentration of hydrogen atoms in the combustion zone, for the property which distinguishes hydrogen atoms from all other species in the flame is their high rate of diffusion. They further developed a theory to account for the burning velocities of gas mixtures in which the combustion mechanism is a relatively simple one Such a theory predicted that the burning velocity of a series of mixtures could be represented by a

product of terms, of which the most important was the square root of the sum of equilibrium free radicals concentrations, each multiplied by its coefficient for diffusion into unburnt gas. A somewhat similar approach to the theory of flame propagation has been made by van Tiggelen[18],Strickland-Constable[19], and Gaydon and Wolfhard.[20]

LUMINOSITY OF FLAMES

The solid particles in flames which give rise to luminous radiation are principally carbon The mechanism of carbon formation, however, is not yet fully understood It is broadly surmised that carbon particles are produced in flames by the cracking of the hydrocarbons. These are produced because cracking outstrips oxidation. Three theories have so far been advanced to account for carbon deposit formation in flames . (*i*) the polymerisation of the C_2 unit and C atom formed by systematic dehydrogenation of the hydrocarbon molecule[21]; (*ii*) the dehydrogenation of the hydrocarbon molecule by the hydrogen atom followed by successive polymerisation of the active residue to the extent of complete removal of hydrogen atoms resulting in solid carbon deposition[22], and (*iii*) the decomposition of the hydrocarbon molecules by pyrolysis, followed by polymerisation (to large hydrocarbon molecules as liquid droplets or in gas phase), dehydrogenation and finally graphitization[23].

Experimentally it has been observed that the addition of additives like CO_2, N_2, H_2O, etc., in critical amounts suppresses carbon formation in flames[24,26] On this basis a view is gaining recognition that hydrogen atoms and radicals participate in polymerisation reactions leading to carbon formation in flames[25,27].

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CARBON FORMATION IN FLAMES

by

MR R VAIDYESWARAN AND DR M S IYENGAR

l Laboratories for Scientific & Industrial Research, Hyderabad-Deccan)

he influence of an additive like carbon dioxide on the iosity of different organic flames is described. It is found he critical rate of carbon dioxide needed to suppress lumi- y decreases with increase in molecular weight for a given .. An attempt is made to correlate critical carbon dioxide with Activation Energy.

luction

he mechanism of carbon formation in flames is of considerable cal importance In furnaces carbon formation is an advantage ncreases the heat-transfer while in internal combustion engines the exhaust gases of turbines it is necessary to avoid carbon for- n and so minimize coking troubles

nfortunately, however, not much is known about the exact nism of carbon formation But this much *is* known, that the osity of flames is due to carbon particles heated to incandescence noke formation is due to the coagulation of the carbon particles ind Outridge[1] studied carbon deposition in equi-molecular mix- of ethylene and oxygen with varying amounts of various diluent ind concluded that carbon deposition was primarily determined e temperature However, this is not completely correct as in cases pressure also has a marked effect, carbon deposition occur- nore readily at higher pressures and being suppressed altogether er pressures The hydrocarbons which are richest in carbon and ally the unsaturated ones like acetylene and benzene most readily t carbon and even methane gives quite a luminous flame and the nce appears to be one of degree rather than of kind. Carbon tion occurs in the flames of many organic compounds besides carbons. The alcohols give less of carbon deposition, with the ion of methyl alcohol which gives a non-luminous flame in air.

Formaldehyde will not give carbon at all while acetaldehyde and acetone burn with quite luminous flames.

Experimental

The apparatus used in these experiments consisted of a modified spirit lamp with a side tube through which an additive like carbon dioxide could be introduced There was arrangement for measuring the rate of CO_2 The procedure adopted was to take a series of organic liquids, burn them and measure the corresponding amount of carbon dioxide needed to make the flame non-luminous Care was taken to use the purest available liquids The data obtained are shown in Table I.

TABLE I

CRITICAL RATES OF ADDITIVE TO SUPRESS LUMINOSITY

Liquid	Critical rate of CO_2 ml./min.
n-Hexane	130
n-Heptane	45
n-Octane	75
n-Decane	50
Ethyl alcohol	43
Iso-propyl alcohol	32
Butyl alcohol	23
Iso-butyl alcohol	23
Amyl alcohol	14

Discussion

From Table I it is evident that the critical rate of additive decreases with increase in molecular weight In a previous paper[2], three possible mechanisms for carbon formation were put forward and it was stated that the more likely mechanism was that the hydrocarbons act as third bodies for the recombination of hydrogen atoms formed in flames and that the heat of recombination of the hydrogen atoms decomposed the hydrocarbons resulting in carbon formation :

$$C_n\ H_m + H + H \longrightarrow C_n\ H_m\ ^* + H_2$$

An attempt was made to correlate the critical rate of carbon dioxide with the corresponding activation energy of each hydrocarbon for decomposition into its radical, for the hydrocarbon series (see Table 2).

TABLE 2.

CORRELATION OF CRITICAL RATES OF ADDITIVE WITH ACTIVATION ENERGY

Liquid	activation energy* Kcal	critical rate of CO, ml./min.
n-Hexane	64	150
n-Heptane	63 2*	45
n-Octane	62 5	75
n-Decane	61 4	50

* Figures obtained by Rice and Rice, "The Aliphatic Radicals," Baltimore, 1935.

Comparison of Table I with Table 2 reveals that qualitatively at any rate there seems to be a correlation between the rates of additive needed to suppress luminosity and activation energy. A likely interpretation of the above observation is as follows. Since larger molecules of the hydrocarbons need less activation energy for dissociation into radicals, smaller numbers of hydrogen atoms need recombine on these molecules to dissociate them, so that correspondingly less amounts of the additive are needed to suppress the important initiating reactions of carbon formation in flames.

From the above Tables it will be noticed that n-heptane shows deviation from the general rule. With the evidence available at present we are not in a position to explain the observation.

Further work is in progress.

Acknowledgement

Our thanks are due to Dr S Husain Zaheer for taking a keen interest in this work and for allowing this paper to be presented today. Our thanks are also due to the Board of Scientific and Industrial Research, Hyderabad-Deccan, for providing a scholarship to one of us (R.V.).

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COMBUSTION OF NON-CAKING HYDERABAD COALS IN A FUEL BED

by

MR R VAIDYESWARAN & DR M. S. IYENGAR

(Central Laboratories for Scientific & Industrial Research, Hyderabad-Deccan)

The influence of carbon dioxide on the ignition and burning out stages of Hyderabad coals is described. The results obtained in a 6-inch diameter combustion pot are correlated to conditions on a chain grate stoker in boilers. It is found that upon introduction of carbon dioxide with primary air the ignition time is increased and the burning out time is decreased.

Introduction

Most of the coals in India are used for steam-raising purposes. But what is not fully appreciated is that not all coals are suitable for these purposes The factors that have to be taken into consideration in the choosing of coals for steam-raising purposes are ease of gasification, non-caking characteristics, high fusion point of ash and the non-clinkering nature of coals. Besides, the mode of firing is also an important factor in attaining the best efficiency in boilers By the proper control of primary air and by suitable recirculation of flue gases it is possible to mitigate the formation of bonded deposits on the heating surfaces of the boilers.

Experimental

The apparatus used in these experiments consisted of a vertical steel cylinder 6 inches in diameter and 19 inches high in which the fuel bed is supported on a metal grate about three inches from the bottom. Primary air was passed upwards from the bottom of the grate. There was an arrangement for introducing an additive like carbon dioxide along with the stream of primary air. The fuel bed was ignited by cotton waste soaked in paraffin placed on top of the bed. The duration of the ignition period and the burning out period for a particular air rate with and without carbon dioxide was obtained. At the end of

the run the residue was removed by hand and the unburnt carbon weighed. The data obtained are presented in Table 1.

TABLE 1

INFLUENCE OF CARBON DIOXIDE ON THE COMBUSTION OF COAL

Air rate 3 75 cu ft./min.
Size of coal 1/2 in

	Ignition time (min)	Burning out time (min)	Total time of combustion (min)	Residue %
With CO_2	40	25	65	4
Without CO_2 .	32	28	60	5

Discussion

Nicholls' work[1] showed that in the combustion of coal on a chain grate stoker there are two distinct stages (i) ignition stage, when the volatiles in coal are emitted and ignited by the radiant heat of the furnace; the ignited plane then travels downwards through the green coal against the air flow until it reaches the grate ; and (ii) the burning out stage when the de-volatilised coal burns down to ash It is during the burning out stage that the sulphur present in coal gets converted to sulphuric acid and reacts with the alkali salts forming alkali-sulphates which condense on the outer surface of the boiler tubes thereby reducing the heat-transfer. The influence of carbon dioxide is to reduce the burning out period and thus minimise the boiler depositions.

Conclusion

With proper addition of carbon dioxide to primary air it should be possible to decrease the burning out period, avoid formation of bonded deposits and establish efficient conditions of combustion on a chain grate stoker in boilers. Further work is in progress.

Acknowledgement

Our thanks are due to Dr. S. Husain Zaheer for allowing this paper to be presented at this Symposium and to the Board of Scientific and Industrial Research, Hyderabad-Deccan, for providing a scholarship for one of us (R.V.).

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DISCUSSION

Participants :

1. Dr. H. G. Kayser, Laxminarayana Institute of Technology, Nagpur (*Chairman*).
2. Dr. S. Husain Zaheer, Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn.
3. Dr. M. R Mandlekar, Commerce & Industries Department, Bombay.
4. Dr. B. S. Kulkarni, Applied Chemistry Department, Osmania University, Hyderabad-Dn
5. Dr. M. S. Iyengar, Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn.
6. Dr. M. G. Krishna, Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn.
7. Mr. R Vaidyeswaran, Central Laboratories for Scientific & Industrial Research, Hyderabad-Dn.

The papers on " Modern Conception of Flames," " Carbon Formation in Flames " and " Combustion of non-caking Hyderabad Coals," were taken together for discussion

Reference was made to the phenomena of " *cool flames* " by one of the speakers (M.R.M.). While conducting systematic investigations into the influence of pressure on the combustion of hydrocarbons it was discovered that although at low pressures ignition did not occur below 500-700°C., on the attainment of a critical pressure, varying with the material concerned and the composition of its mixture with air/oxygen, ignition occurred abruptly in a temperature range below about 370° in which only cool flames were normally observable, an important observation being the occurrence of two pressure minima of ignition, one at 280-330°C., and the other at about 340-370°C. Further, increase of working pressure in the low temperature region much beyond the indicated boundaries, made the dual character of the ignition less obvious, until at a third critical value ignition became a single-stage phenomenon, marked by great violence. This type of ignition closely simulated the phenomenon of knock in internal combustion engines and there was an exceedingly close relationship between

the pressure requisite for spontaneous ignition at low temperatures and the critical compression ratios inducing knock in internal combustion engines.

A point of view was expressed (S.H.Z.) that it was not necessary to carry out *experiments on homologues* as what mattered in carbon formation was the ratio of carbon to hydrogen in a given compound and study could be made on the flames of liquids belonging to different series but having the same carbon/hydrogen ratios. It was however contended (M S I.) that to attribute carbon formation to carbon-hydrogen ratio alone was over-simplification and that carbon formation was a complex mechanism The decomposition of molecules into radicals and the polymerisation reactions of the radicals lead to carbon formation in flames. The decomposition of liquids to radicals varied for different series. While two liquids belonging to different series may have the same carbon-hydrogen ratio, their dissociation to radicals may take place differently, though for a given series the decomposition pattern may be the same. It was therefore necessary to study the flames of different homologues

A question was asked (S H Z.) regarding the *relation of carbon formation with bonded deposits formed in boilers* In reply it was stated (M.S.I.) that bonded deposits were formed by conversion of sulphur in coal to sulphur dioxide, sulphur trioxide and sulphuric acid which then reacted with the alkali present in ash to form alkali sulphate which condensed on the outside of the boiler tubes. Like the mechanism of carbon deposit formation in flames the boiler-deposit formation was also a chain reaction It was further stated (H.G.K.) that the deposit reactions took place under unfavourable conditions The introduction of carbon dioxide along with primary air probably inhibited the chain reaction leading to bonded deposits. It was probably for this reason that part of flue gases were recirculated along with primary air in boilers in industrial practice.

In reply to a question (M.G.K.) on *the economics of circulating carbon dioxide* along with primary air, it was stated (M.S.I.) that this had not been worked out, but since in industrial practice it was the flue gas which was recirculated the process would appear to be economically feasible.

SYMPOSIUM ON FATS & OILS

Edited by

Dr. K. T. ACHAYA

President: Dr. S. A. SALETORE, Assistant Director,
Central Laboratories, Hyderabad-Dn.

THE FUTURE OF THE EDIBLE FAT INDUSTRIES IN INDIA

by

DR. S. A. SALETORE

(Central Laboratories, Hyderabad-Deccan)

I have taken up this subject, *viz.*, "The future of the edible fat industries in India" with some amount of trepidation because the subject is vast and hence difficult to deal with within the compass of a short paper. My reason for selection of this topic however is that we oil chemists are usually engrossed in our day-to-day work on specific problems and rarely have opportunities to discuss problems in their entirety; so this occasion appeared to me to be particularly appropriate. Possibly, the fact that I have devoted a major part of my life to this industry may have also had something to do with my choice of the subject.

Before I go any further, I think it is well that I clear any possible misconceptions regarding the title of this paper. The future of anything, let alone 'fats,' is always uncertain and in these uncertain times it is doubly so; hence he would indeed be a bold man who would dare to forecast anything. What I intend doing today, therefore, is not to prophesy anything, but simply to draw your attention to the existing position of the edible fat industry, indicate some of its main drawbacks and suggest what could and should be done if the industry is to come into its own. By 'edible fats' I mean all saponifiable oils and fats, irrespective of origin, commonly used for edible purposes.

Now, to come to the subject proper, broadly speaking we can divide edible fats consumed in India into three main categories:—

i. vegetable oils like sesame oil, coconut oil, mustard oil, and groundnut oil;

ii. ghee fats;

iii. processed fats, mainly vanaspati.

The classification would be quite different in Europe or America, but here we are concerned with our own country.

Coming to think of it, one interesting thing about edible fats in India is that so far as the consumers are concerned, there is no scientific appraisal of the virtues and qualities of each of these types, based on merit. Ghee is considered to be the best fat for all purposes, and if ghee were available at the same price as say sesame oil, I am quite certain that no housewife would even consider sesame oil, except perhaps as a hair oil. Vegetable oil is the poor man's food. This has been the position all these thousands of years, and it is only recently that the position has been challenged by the arrival of the new product of science commonly known as 'vanaspati.' My main point is that no effort has been made to evalute each of these products on its own intrinsic merits, based, firstly, on the requirements of the human body, and secondly, on the suitability of same for the type of food eaten Sooner or later, these two aspect will have to be gone into, if the edible fat industry is to develop along the right lines

Now to come back to our subject, the most important fact, increasingly becoming apparent, is that the consumption of edible fats in India is much below healthy nutrition levels That this is so will become clear from the figures given below for the annual consumption of edible fats under all counts in different countries .—

United Kingdom	1934	44 4 lb	per head
United States of America	1934	45 3 lb.	do.
India	1944	7 9 lb	do.

7 9 lb. per annum per human being in India works out to a consumption of about 0 34 oz per day as against a minimum requirement of 2 oz. per day for normal healthy life, according to nutrition experts This means that we shall require an additional 1 66 oz. of fat per person per day, that is to say an extra 37 8 lb. per year, or nearly 5 times as much as is consumed today For 350 million people in India today, this works out to an extra 3 65 million tons of edible fats as against the present consumption of about 1 23 million tons With the rapidly improving standard of living of the masses, they will want more and more fats and how to find this extra quantity is indeed a serious problem. As a matter of fact, this shortage of edible fats is already being felt. The problem is no doubt one primarily for agricultural experts and diary experts to solve but I think that we, oil technologists, can also help to a certain extent, and possibly more quickly and assuredly than the others.

To my mind the following methods suggest themselves :—

1. By expression of oil from cotton seeds This should give us at least 100,000 tons of oil. Considering that cotton seed oil is the main edible oil in the U.S.A. it is surprising that we in India should have neglected it so far. To my mind crushing of cotton seed is inevitable in India.

2. By making use of the highly unsaturated fatty oils, for example linseed oil, which all along have been considered non-edible and fit only for the production of paints and varnishes. I too was of the same opinion till I went to Nagpur and found that the majority of people there eat only linseed oil The amount of same consumed for edible purposes is about 30,000 tons in the province of Madhya Pradesh alone. I have tasted food cooked with linseed oil and found that except for an odd taste to which one is not accustomed, there seems to be nothing wrong with it. If the oil were to be refined, I am sure that this taste will be much improved. Perhaps the best way in which it could be utilised however would be to refine and slightly hydrogenate it, to reduce its content of highly unsaturated glycerides. Since linseed oil contains about 10 per cent saturated fatty acids, 10 per cent. oleic acid, 42 per cent. linoleic acid and 38 per cent. linolenic acid, partial hydrogenation should be able to give us a product consisting mainly of oleic, linoleic and saturated acids bringing it on par with other edible fats. My reason for suggesting this is that linseed is the only seed other than castor which we are producing in excess and which we have been exporting in large quantities.

3. One other way of obtaining more oil would be to get more oil out of the seeds crushed in India. The oil lost in the oil-cakes according to my calculations is 1,92,000 tons from 1,848,000 tons oil-cakes for the whole of undivided India This is based on 738,000 tons of ghany oil-cakes containing 103,320 tons oil (14 per cent. oil content) and 1,110,000 tons oil-cakes produced in expellers and hydraulic presses, containing 88,800 tons oil (8 per cent oil content). As a good part of this oil goes into the soil for manuring purposes it is clearly a dead loss. There are two ways of recovering this oil (*i*) by the use of more efficient milling machinery, and (*ii*) by solvent extraction. Ordinary oil-pressing machinery leaves anywhere from 7 to 9 per cent. oil in the cake, while high-efficiency American machinery like the Super duo twin-motor expeller can bring down the oil in cake to 4 or 4½ per cent.

The main obstacle in the way of our employing such machinery is the high cost of same and so until and unless we are able to fabricate same in India itself, I do not see much chance of employing this method. But conditions in India are such that even the ordinary expellers made here are crude compared with the same type of expellers imported from abroad. Hence it is too much to expect that private enterprise will be able to manufacture a high quality super-efficient type of expeller in the immediate future. To my mind the first thing necessary is to make better quality standard expellers, and in this active help from Government is essential

Regarding solvent extraction, it is most unfortunate that the plants set up in India have all been failures Space and time do not permit me to go into the reasons for these failures, but if one were to go into the matter carefully, as I have done, it will be seen that not one of these plants had a single favourable factor. If machinery were to be specially designed for Indian conditions, with a full appreciation of the difficulties regarding climate, lack of the usual solvents, etc, there is no reason why solvent extraction should not be a success. But if the same mistakes are committed, as I am very much afraid they are going to be, I shall not be surprised if some more solvent plants are set up only to go into liquidation later on. What is more natural than that oil chemists should be blamed ? I would therefore entreat oil chemists in India to be doubly careful about sponsoring solvent-plant projects.

If solvent extraction were properly established, we should be able to recover well over 1,73,000 tons of oil from 1,848,000 tons of oil-cake.

In view of the hazards of commercial exploitation, it is most unlikely that private enterprise will be able to start this industry in India in the way it should be done. Hence if solvent extraction is to be established in India, it is very necessary that Government sets up first a model factory as was done in the case of the soap industry in Madras Presidency.

4. There is another way in which more edible fats can be made available to the nation. As we all know, large amounts of edible fats are now being used in industry for non-edible purposes, for example for the manufacture of soap. These edible fats could easily be weaned and replaced by non-edible fats and other materials if suitable substitutes can be found. Other countries have done it and there is no

reason why we cannot do the same. One way would be to make use of the vast untapped resources that we have all along our long coast-line and develop the fish-oil industry followed up by hydrogenation of the fish-oil. Hydrogenated fish oil can replace to a certain extent edible oils used in industries manufacturing non-edible products. Similarly, castor oil if dehydrated can replace linseed oil in the paint and varnish industries thereby releasing linseed oil for edible purposes. Greater use could be made of a variety of miscellaneous oilseeds like neem, tobacco seed, custard apple seed, karanja, kusum and so on by extracting the oil from same for use in the soap industry Developing the mutton tallow industry, I need hardly mention, would also greatly help the soap industry and indirectly save some of our edible oils.

At the present moment 55,000 tons of groundnut oil, to mention only one instance, are being used by the soap industry

Having considered the overall position of edible fats in India, let me now take up one by one the three categories mentioned by me earlier First, we have vegetable oils Vegetable oils constitute the bulk of the edible fats consumed in India, amounting to approximately 540,000 tons out of a total production of 1,144,500 tons of oil produced in this country. The details are as follows —

400,000 bullock-driven ghanies and small-scale establishments produce	363,000	tons of oil
3,000 expellers and 100 hydraulic presses produce . . .	781,500	do.
	1,144,500	do.

In this connection it is worth noting that approximately 67 per cent of the edible oil is being produced in ghanies. Though undoubtedly ghanies are inefficient compared with modern oil milling machinery, in all probability they will continue to exist in India for many years to come. The Industrial Advisory Panel on vegatable oils of the Government of India, of which I have had the privilege of being a member, was of the opinion that ghanies have a place in the economy of the country and that while crushing of oilseeds in modern machinery was best for oils meant to be used for further processing in factories, ghanies served a useful purpose in supplying small quantities of edible oil directly to consumers in their immediate neighbourhood. This is understandable, as after all the first essential in an edible oil is its

fragrance, and ghany-pressed oil is definitely superior in aroma to oil pressed in more efficient machinery at much higher temperatures. This is particularly so in the case of mustard oil, which is an important edible oil of India. I well remember how some years ago in Calcutta, Mr. Weill, the German Manager of Krupp India Trading Co., conducted several large-scale trials to replace ghanies by expellers for producing mustard oil, but without any success. The expeller oil lacked the rich flavour of ghany oil. The same is the case with other oilseeds Then again, ghany-pressed oils not only have a superior aroma but are likely to contain more of the non-glyceride constituents like vitamins and phosphatides which have definite nutritive values. Hence if there is to be progress, instead of trying to do away with the village ghany it would be much better if we could evolve better types of ghanies or similar small-scale machinery suitable for cottage industries and preferably worked by means of electric power. I believe some such machinery is being worked satisfactorily in Japan.

As regards power-driven oil mills, though we have about 700 factories registered under the Factories Act, only a few of them are big ones, the majority of factories being small concerns with an average of 2 to 3 expellers Their main defects are —

i use of inefficient types of Indian-made expellers ;
ii. insufficient cleaning of seeds, and very often no cleaning ;
iii. insufficient milling or no milling ;
iv. no scientific control of any sort.

The inefficiency of Indian-made expellers has already been referred to earlier in this paper. The poor quality of the machines is due to the fact that most of the workshops which fabricate these are small shows with insufficient capital, inferior machinery and hardly any qualified designing staff When I was a member of the Planning Committee of Central Provinces and Berar, I had suggested that Ordnance Factory workshops could easily be utilised during peace time for fabrication of expellers, and I understand that the Jubbulpore Gun-carriage factory subsequently did manufacture some. But as far as I know the idea was not properly developed later on, and I do not know what has happened since.

The necessity for cleaning seed is little understood in India, the proprietors of small oil mills and even some of the big ones being under the impression that cleaning is only a waste of time and money. I

have personally tried experiments and found that the higher wear and tear of the milling rolls and expeller worms is partly due to the sand and grit particles mixed with the seeds. Addition of a cleaning system considerably reduces repair and renewal costs Admixture with other seeds is quite common though it is only occasionally that we come to hear of it. The unfortunate deaths in Simla due to the presence of argemone oil in mustard oil is one such tragic instance.

It is generally believed that oil milling is a very profitable business, but actually this is not so Except during wartime, when most factories made huge profits, ordinarily during peace time the margin of profit is very narrow and this is true not only of India but of other countries also. Hence if the oil milling industry in the future is to do well and not merely exist, much more efficient working is necessary

Next to the oil milling industry, we have the ghee industry It has been estimated that India produces annually 10 million maunds or 3,57,000 tons of ghee and 360,000 maunds or 12,860 tons of butter, both of which are becoming scarcer and scarcer every day and more costly I do not propose to deal with the subject in detail today as a separate paper on this subject is featured in the programme I would however draw attention to one point considering the magnitude of the industry it is extremely surprising that no attention is being paid by Government to the quality of the ghee I am not referring to adulteration which is only too well known, but to the fact that even the genuine ghee sold in the bazar is far from being what it could be in aroma and taste. The Agmark scheme of Government, though well-intentioned and though it may serve the purpose of standardising quality, to my mind is only tackling the issue at the wrong end. There is not much point in standardising when there is no control over production. If only Government were to tackle this matter at the source, it would be a great blessing.

I now come to the subject of 'vanaspati,' the third important edible fat we have in this country. As against 10 or 11 factories before the war, there are now 50 or 60 factories, some still under construction. The production of vanaspati, which was 1,13,000 tons or so in 1939, went up to 1,40,000 tons by 1946 and is expected to go up to 4,00,000 tons when all the new factories are working Vanaspati has come into the limelight during the last few months, since Pandit Thakurdas Bhargava's bill is to come up for discussion shortly before the Indian Parliament, proposing to ban its production As a result vanaspati is having

a lot of publicity both for and against it. While this paper is not concerned primarily with the merits of the case, since it is an extremely important matter for the future of the industry, I feel I cannot but refer to it and I shall do so briefly, in as impartial a manner as possible.

Now what is vanaspati ? It is nothing but a slight modification of one or other of our common vegetable oils, the oil mainly used being groundnut oil As an article of food, in terms of calories there is hardly any difference between vegetable oils and vanaspati. But it is costlier, which is a point against it It however keeps better than vegetable oils and is marketted in clean tins, which are points in its favour. The fact that it contains more of the higher-melting stearic acid is made much of by its opponents, but to my mind this argument completely ignores the fact that lard and tallow, not to mention chocolates, which are all high in stearic acid, are consumed daily in western countries without any ill effect. For all I know, a certain quota of stearic-acid glycerides may be beneficial to the human body. Its lack of vitamins, phosphatides and other non-glyceridic matter is certainly a point against vanaspati. But when used as a cooking medium this does not seem to be important as it is doubtful if the vitamins in any kind of fat, whether ghee, oil or vanaspati, will survive the drastic treatment meted out during cooking, particularly frying. Then again, the average Indian is not entirely dependent on his cooking oils or ghee for his fat-soluble vitamins, these being available to him in much larger quantities from other sources.

The absence of the more highly unsaturated fatty acids like linoleic acid found in vegetable oils is in my opinion a more important consideration as there is a possibility that these acids are required by the human body and may not be synthesised by it. The real fact is, we do not know. A few experiments on mice are not enough. At the same time, since most Indians even if they are non-vegetarians eat vegetables, and since these vegetables do contain small quantities of the unsaturated acids, the possibility that our bodily requirements of unsaturated fatty acids are being met with from these sources cannot be ignored.

Lastly, we have the presence of iso-oleic acid in varying proportions in vanaspati, the eating of which is supposed to be followed by all sorts of dire consequences. Here again, the fact of the matter is that we know very little about its action on the human body. I

would not say that it is harmless, nor would I say that it is harmful. All that can be said is that hydrogenated oils have been consumed in Europe and America for over a quarter of a century without any apparent ill effect and ordinary canons of justice require that the charge should be proved before calling them criminals.

As against all this, vanaspati has certain definite advantages over both oils and ghee, in that it is more suited for deep frying, giving a less greasy and more crisp product, and in that it is more suitable for certain types of processed foods like biscuits, cakes and pastry The importance of this does not seem to have been sufficiently understood in this country

There is yet another point in its favour which is very little stressed even by its supporters for obvious reasons, which in my opinion is perhaps its most important advantage but also its disadvantage I refer to the ghee flavour of the flavoured varieties. Now one of the main factors contributing to good digestion of any food is that it should be appetising and pleasing to the taste and smell ; hence so long as the average Indian likes the taste of ghee and relishes food smelling of ghee, so long will the ghee flavour remain an important attribute of vanaspati. The value of this psychological factor is little realised in this country. If for example genuine ghee were completely deodorised, I am quite certain people will not enjoy food cooked in it as much as they do food having the fine aroma of ghee.

From all the above it is clear that vanaspati has merits as well as demerits, and that each of the three types of fat, vegetable oil, genuine ghee and vanaspati, has its own specific advantages for specific purposes. The maximum benefit will be derived by using all three.

Now to come to our main question, what is the future of the vanaspati industry in India ? I personally feel that the immediate future is bleak while in the long run it is bright. I am pessimistic about its immediate future for a number of reasons. Firstly, there has been a rapid growth of the industry during the last few years without care or consideration for either industrial economics or efficiency. A large number of factories have sprung up with machinery purchased at inflated prices, and not a few of them are being worked with less than the minimum of scientific control. I well remember an instance of an ordinary *mistry* being put in charge of operation of a hardening plant on Rs. 600/- or so simply because he had twiddled a few valves

in some other factory while M.Sc.'s and Technological B.Sc.'s were being refused even Rs. 150/-. With such persons in charge progress is not possible Then we have Government control over prices of vanaspati without at the same time controlling prices of raw oils, etc. On the other hand raw oils are being used in vanaspati factories without any checking of quality Is it surprising that more than one factory has produced vanaspati containing as much as 15 to 20 per cent. of castor oil ? Some of the factories have not even taken the elementary precautions necessary to prevent explosion of the highly explosive gas hydrogen. I very much doubt whether most of them even know what these precautions are But, worst of all, what is undermining the healthy growth of the industry more than anything else is the basis on which the industry as a whole exists today I refer to the ghee adulteration business Vanaspati has a perfectly sound case for standing on its own merits, but unfortunately as things are in India today, vanaspati is not allowed a fair chance by its manufacturers to build up a slow but steady legitimate market Vanaspati trade up till now has been built largely on the illicit adulteration of ghee, bringing rich profits to some, and that is why so many factories have sprung up. I am not saying that the vanaspati manufacturer has any hand in this adulteration business, but he cannot on this account be absolved of all blame, for he knows well enough where the vanaspati goes If therefore, public agitation gets stronger and stronger and bills like the one wanting to ban the production of vanaspati are proposed, the blame rests primarily on the vanaspati manufacturer himself. As things are today, the greatest enemy of vanaspati, and the one who is hindering the healthy growth of a new industry with vast potentialities, is the vanaspati manufacturer himself, by reason of the rotten foundations on which the industry has been built.

Adulteration of ghee is of course no reason for banning the production of vanaspati , one might as well ban the supply of water because the milkman uses it for adulteration of milk, or ban the sale of matches because *goondas* use them for setting fire to houses.

I would again repeat that the industry can well stand on its own merits, but before it can do so, industrialists will have to realise that the long-term prosperity of the industry does not rest on the adulteration trade and take active steps to prevent the use of vanaspati for adulteration purposes. Till then the industry will have to face more and more

restrictions brought about by public agitation, some of which may quite possibly be unjust and throttle the healthy growth of the industry.

While considering the future of this industry, I personally feel that the industry is still in its infancy, and that a good deal of progress is possible. It would therefore be worth our while to examine these possibilities.

There can be no two opinions on the point that vanaspati as produced at present is only an imitation of ghee, and a poor imitation at that. There is no reason why scientific research should not be able to produce something better. Vanaspati today contains mainly oleic and stearic acids with a certain amount of iso-oleic acid. Ghee contains about 5 per cent. lauric acid, 8 per cent. myristic, 30 per cent palmitic, 9 per cent. stearic, 35 per cent. oleic, 8 to 9 per cent of low molecular weight saturated acids and small quantities of unsaturated acids other than oleic. Addition of coconut oil can give us the saturated fatty acids ranging from C_8 to C_{14} while cottonseed oil can provide us with palmitic acid. How to get the still lower fatty acids is a problem worth investigating. To produce a genuine ghee flavour is another of our problems. The main defect in present-day vanaspati is that the flavour does not persist so well in the cooked food as it does with ghee. The lack of vitamins is another defect, which however is more easily remedied by simple addition of same. All these problems will I am sure be tackled by the oil chemists of India in days to come.

As regards the technical working of the factory, from what I have seen personally, much progress is possible, firstly, in cutting down losses particularly in the refinery, and secondly, in speedingup operations thereby cutting down working costs. The utilisation of waste products also remains to be tackled.

Before I close, I would like to refer to one other aspect of great importance both to the consumers as well as the producers of edible fats in India, namely, the suitability of different types of fats for the different kinds of edible foods prepared in India. In western countries a great deal of research has been done on the choice of fats for specific classes of edible products, and the buyers make use of the knowledge and buy exactly what they want. Their choice is governed by such things as (*i*) the structure of the baked product, (*ii*) the relation of the fat to the leavening process, (*iii*) shortening value, *i.e.*, the ability of a fat to lubricate and weaken the structure of the baked product, (*iv*) creaming

quality, (*v*) stability of the fat, in the case of packaged goods, and (*vi*) the behaviour of the fat in commercial deep frying.

In India no such fine distinctions are known and till now ghee has been considered the best fat for all purposes, and that ended the matter. Whether it is Bombay *halva* or Bengalee *rasagulla*, the Madrasee *dohve* or Mysore *pak*, the Punjabee *nankhatai* or the Hyderabad *biryani*, no special characteristics have been specified for the fat used in the preparation. It may well be that if research were carried out it would be found that what is best for one type of eatable is not perhaps the best for another type, and that with a proper choice of fat we shall have better and more lasting eatables than at present Research along these lines may yet show that the superiority of ghee is overrated and that vegetable oils, refined oils, slightly hydrogenated oils, vanaspati ghee, superglycerinated shortenings, all have their own specific advantages for specific purposes We have a long way to go but if the oil chemists of India get out of the beaten track and devote themselves to the task, vast new avenues lie before them.

DISCUSSION

The following took part in the discussion —

Dr. J. S. Aggarwal, National Chemical Laboratory, Poona
Mr. H. H. Mathur,National Chemical Laboratory, Poona
Prof. B. N. Banerjee, Indian Institute of Science, Bangalore.
Mr. S. S. Acharya, College of Agriculture, Hyderabad-Deccan
Dr. S. Husain Zaheer, Central Laboratories, Hyderabad-Deccan.
Dr. K. Ramachandran, Central Laboratories, Hyderabad-Deccan.
Dr. K. T. Achaya, Central Laboratories Hyderabad-Deccan.
Mr L. M. Srivastava, Central Laboratories, Hyderabad-Deccan
Mr. J. Lakshmikantham, Central Laboratories, Hyderabad-Dn.
Mr N. Bhojraj Naidu, Central Laboratories, Hyderabad-Dn.

The production of fat from yeasts and other micro-organisms, attempted on a large scale in Germany during the war, was put forward for consideration (K.R.), and supported with mention of the earlier theoretical work of Reichel and Schmid, and of Haehn and Kinttof, on yeast fat (K.T.A.). Details of the two processes commonly used were described (J.L.) ; yeast-like organisms producing fats are *Oospora* (*Oodium*) *lactis*, *Endomyces vernalis*, etc., while moulds which produce fats belong to the families *Citromyces*, *Penicillium*, *Aspergillus*. In the floor process, sawdust

was the medium and fat-production was usually maximal in about eleven days, but sugar utilization was not as complete as in the pan process which usually took just seven days, the name being derived from the shallow pans used. Sulphite waste-liquors containing sugars could be used as nutrient media ; the fats formed contain lauric, palmitic, oleic and linoleic acids, while the phospholipids contain lecithin, cephalin ergosterol and zymosterol. It was stressed that the processes would probably only be used in time of national emergency , the speaker (S.A S) agreed and suggested that sources of fat already available, *e.g.*, fish oils, could preferably be tapped.

The utilization of linseed oil for edible purposes mentioned by the lecturer, came in for some discussion ; some (H H M , J S.A.) considered that this oil was best used in paints, and as the speaker (S A S) remarked it was a question of food before before paint, or vice versa. The use of certain non-edible fats for soap manufacture would wean edible oils now being used for this purpose to proper ends thus the indigenous pisa fat, containing 92 per cent. of lauric acid, could substitute for coconut oil (J S A), while the local " hundi " oil could also be used for soap making (N.B.N)

Solvent extraction of oilseeds, much practised in technically advanced countries, was considered by several speakers (H.H M , J.S A) to be unsuitable for India on account of prevalent high temperatures, the lack of a solvent source and high initial costs. In reply to an enquiry (L.M.S.) no actual figures were forthcoming for the costs of the operation either for the batch or continuous processes of extraction. It was stressed (B.N.B.) that the residual cake, containing oil, was used in India for feeding milking cows and draught bullocks, and that the buffaloes of Kathiawar fed heavily on cottonseed gave high yields of milk , however it was remarked (K.T.A.) that the work of Krizenecky had shown that the fat of milk was largely proportional to the protein content of the feed, so that no great harm was done by reducing the oil content of cake to a low figure ; the speaker (S A.S) remarked that in the U.S.A. and Holland, cattle were fed on compounded feed consisting of solvent-extracted oilcake, molasses, etc. without ill-effects, and that human beings were probably in more urgent need of the oil in the oilcake than cattle.

The proper grading, storage and milling of oilseeds were the subject of some attention. Poor seed, whether broken, mouldy or shrivelled,

gave oil of poor quality, while with fresh, whole seed, oils of acidities as low as 0.1 per cent. (as oleic) could be obtained (B.N.B.) ; the storage of seeds in Indian oil mills was poorly done, and rotation of storage-bags would prevent heat-generation and fire-risk by facilitating aeration (N.B.N) ; cleaning of seeds was essential since dust reduced yield by absorbing oil (H.H.M). Pre-heat-treatment of fresh seed even by simple sun-drying was suggested (K.T.A.) as essential to arrest enzymic decomposition of oil. The Skipin process of seed-meal cooking, leading to incidental oil recovery, was mentioned as likely to be of some interest for Indian conditions (K.T.A., H.H.M.).

The question of the production and digestibility of hydrogenated fat (vanaspati) was raised by several participants in the course of the discussion. In answer to a query regarding selectivity of catalysis (S.S.A.), it was pointed out (H.H M.) that nickel from nitrate or formate, compared to that from sulphate, led to minimal iso-oleic acid formation ; nickel was almost universally used on account of cheapness and neither platinum nor palladium was likely to supplant it. Figures for the percentage of iso-oleic acid were given (B.N.B) as lying between 6 and 26 per cent., averaging about 10-12 per cent., though the validity of the present method of determining this figure was doubted (K T.A.). One speaker (S S A.) considered that the presence of stearic acid in hydrogenated fat was not as injurious as that of iso-oleic acid, though this was doubted by another (N.B.N.) ; a third (K.T.A) considered that the relative, rather than the individual, proportions of various glycerides would probably condition digestibility, and also pointed out that the essential linoleic acid was still substantially present in hydrogenated fats of fairly high melting points and low iodine values.

Ghee-making was a cottage industry and proper methods should be taught in village homes if improvement in the product were desired (B N B., H H.M.). The present Agmark standards were better than no standards at all, and as regards adulteration of ghee, stern measures should be taken to check it (B.N.B.). It was pointed out that a large part of the present production of hydrogenated fat was utilized for the adulteration of ghee (J S.A , B N B.) which would continue as long as the prices of the two products were so disparate (S H.Z.) ; in Uttar Pradesh, *e.g* , it was found during a survey that the consumption of " ghee " was four times that of its legitimate production, but it was useless to run down the existence of an industry like hydrogenation for which there was a real need, and better to restrict the consumption of

ghee to say mothers and to children (S.H.Z.). The speaker (S.A.S.) remarked that the chemist could do little about it, it was for Government to enforce its existing legislation with more vigour.

The segregation of glyceride fractions by processes analogous to "winterising" was mentioned (H.H.M.) ; the speaker (S.A.S.) thought it was not likely to be of use in its original sense since oil in India was used not as a table or saladoil but for cooking purposes.

CASTOR OIL AND ITS GEL

by

DR. J. S. AGGARWAL

(*National Chemical Laboratory, Poona*)

The castor plant, known botanically as *Ricinus communis*, belongs to the natural order Euphorbiaceae It is generally believed to be native to North Africa and probably also to India. In tropical countries, the castor plant achieves the dimensions of a small tree and may attain a height of 20-30 feet. In cooler countries it becomes a shrub or bush 8 to 12 feet high, and in localities where frosts occur it is a herbaceous perennial. The seeds vary very much in colour, size and shape but are usually oval, flattened on one side and of mottled-grey colour. It is sensitive to frost and is therefore only adapted to warm climates or where the summers are sufficiently long to mature the seed A fair amount of moisture and rainfall after sowing is essential to ensure good germination, but after the root system has developed less moisture is needed. The soil best suited to the castor plant is a rich, well-drained sandy or clayey loam, or any land that produces good wheat or maize. Deep ploughing and harrowing are essential. Castor cake itself is *the* most valuable manure for supplying the nitrogen, potash and phosphoric acid that the plant requires.

The castor plants may be large-seeded or small-seeded The former are more prolific in the yield of seeds and the oil obtained from them is suitable for lubrication and industrial purposes , the latter yield a finer oil, used in medicine.

India is the largest producer of castor seed and enjoys almost a monopoly in the world trade in this product It is also cultivated in Brazil, the United States, Manchuria, Java and Indo-China. The average production of castor seed in India during the years 1934-44 was 1,39,000 tons per annum. Hyderabad (Deccan) is the largest producer of castor seed ; Uttar Pradesh, Madras, Bombay and Mysore follow.

Castor seed is interesting for at least three reasons · (*i*) it contains a fat-splitting lipase or ferment which can be commercially used for

splitting not only castor oil but most other oils and fats ; (*ii*) it contains a poisonous principle, ricin, which is a water-soluble protein , it is extremely poisonous but at 70°C. readily coagulates to an insoluble form losing its poisonous properties ; (*iii*) the peculiar character of the oil, which is practically insoluble in petroleum ether but quite soluble in alcohol.

Castor oil has the highest specific gravity of all the common oils, the figure being 0 963. It has a high acetyl value (150) and low iodine value and is the most viscous of all the vegetable oils. Its constituent fatty acids, as percentages, are ricinoleic acid 85, oleic acid 9, linoleic acid 3, stearic acid 3, and dihydroxystearic acid 0 3 It contains a high percentage of ricinoleic acid and hence a large proportion of the simple glyceride triricinolein It is the presence of ricinoleic acid which makes castor oil so useful in various fields

Three grades of straight castor oil are recognised in the trade (1) Pharmaceutical, (2) Firsts, (3) Seconds. The seeds, which contain 35-55 per cent. oil, are screened to remove sand and coarse impurities. They are then passed to cage or stave type of presses and pressure is applied in two or three stages according to the system in use The oil flows fairly freely The pressed seeds, which contain about 12-14 per cent. oil, are passed to solvent extraction plants The usual solvents used are benzene and trichlorethylene Experiments on the use of alcohol for the extraction of castor oil are also in progress. The refining is done by various decolorizing earths and the oil is filtered through filter presses and finally bleached in sunshine. Castor oil has been refined so as to reduce the free fatty acids by treatment with the requisite amount of alkali and then agitating with fuller's earth, when the latter substance absorbs the soap stock and free caustic alkali[1]. Another method[2] has been to dissolve the castor oil in solvents like benzene and toluene and to then neutralize free fatty acids with an aqueous solution of alkaline hydroxide or carbonate and to reflux the mixture for sometime. The precipitated soap is removed and the oil is washed until the wash water is neutral. The solvent is distilled off and the oil dried.

Employment and Uses of Castor Oil

Castor oil is a non-edible oil. It is however used in medicine being a purgative, which action must be ascribed to the presence in

it of ricinoleic acid. It is also used for skin infections. It is extensively employed as hair oil.

Castor oil on saponification with caustic soda gives a soft soap, which is very soluble in water though the lather is not of long duration. Views on the wetting power of castor oil soap are however divided. Shirolkar and Venkataraman[3], and Sadgopal[4] find that the soap of castor oil, rich in ricinoleic acid glyceride, has very little wetting power, but Young and Coons[5] mention that ricinoleic acid salts, having a hydroxyl group and a double bond, are very good wetting agents and are very soluble. Castor oil is not much used in soapmaking ; it is only used as an ingredient of transparent soaps

Castor oil is much used in the manufacture of Turkey red oil which is the product of its sulphonation and sulphation. As is well known, sulphuric acid mostly acts at the hydroxyl group of ricinoleic acid, to form

$$CH_3.\ (CH_2)_5.\ \underset{\displaystyle O.SO_2.OH}{\underset{|}{CH}}.\ CH_2.\ CH{=}CH.\ (CH_2)_7.\ COOH$$

Turkey red oil finds extensive application in the textile industry for the softening of cotton goods and also as a dyeing assistant in neutral or slightly alkaline dye baths, but is readily decomposed in acid dye baths. It is appreciably stable to hard water, but sometimes causes considerable difficulty when used with hard water owing to the formation of insoluble sticky calcium salts. Its instability in acid dye baths has led to the manufacture of products such as sulphated fatty alcohols, fatty acid amides, esters, etc. It also finds application in metal polishes, cosmetic manufacture, pigment wetting for paint production, and water-pigment emulsification, and is used in conjunction with pine oil and cresylic acid for disinfecting purposes. For purposes of calico printing, Turkey red oil is used to oil the cloth initially in order to give brightness and clarity. It is especially employed for the printing of goods of better quality, like chintz, crepe and organdie.

Castor Oil as a Lubricant

A lubricating oil should have a high degree of oiliness and a low coefficient of static friction. The viscosity of the lubricant should also change very little with change in temperature, *i.e.*, the viscosity index of the oil should be high. Owing to its statisfying the above exacting

requirements to a considerable extent, castor oil is regarded as one the best lubricants known and has in the past been employed to a considerable extent in aeroplanes engines As the production of mineral oils in India is very small, investigations were undertaken by Aggarwal, Chaudhry, Mukerji and Verman[6] for the utilization of vegetable oils as lubricants in internal combustion engines. These investigators have found by bench engine tests that blends of refined castor oil and groundnut oil or rape oil stabilized with α – naphthylamine behave as satisfactory lubricants for all types of motor vehicles and light buses These results were further substantiated by actual service conditions As a result of these investigations substantial amounts of vegetable oil lubricants and their blends with mineral oils were used in this country during the last war. Refined blown castor oil also gave satisfactory results when employed as a lubricant in heavier types of buses Castor oil has also been used successfully in the preparation of cutting oils.

Another important use of castor oil is in the manufacture of automotive hydraulic brake fluids Castor base type hydraulic brake fluids have the widest use in the market Experiments on their formulation were made at the Harcourt Butler Technical Institute, Kanpur and also in the laboratories of the Council of Scientific and Industrial Research, Delhi.

Heat Treatment of Castor Oil

The changes which castor oil undergoes when subjected to heat treatment are quite interesting. Recently, Bhasin and Aggarwal[7] have studied the effect of heat on castor oil. The changes in various characteristics are very little when the heating is up to 200°C., but at 275-300°C. the specific gravity, viscosity and the acid and saponification values increase while the iodine and acetyl values are reduced to a great extent. These changes are even more marked when castor oil is heated in presence of air, so much so that after four hours heating at 275-300°C. castor oil changes to a gel. Roy[8] studied the changes in castor oil when heated at 140°C in the presence of oxygen and nitrogen. The viscosity, iodine number, acid number and refractive index were found to increase in the presence of oxygen. Similiar work has been done in China[9] by heating castor oil at 240-290°C. for 1-6 hours at atmosphere pressure. The heating of castor oil to a high temperature leads to the formation of dehydrated castor oil.

The first to put the production of dehydrated castor oil on a sound commercial basis was Scheiber[10] in 1931 But the use of castor oil as a coating material must have been known earlier because in the older text books it was included among the drying oils. Thus Brundt calls it a drying oil, and Livachi and McIntosh include it among " drying oils other than linseed." The Mappe Claviculae, quoted by Sir C. L Eastlake, say · " This oil was used as a varnish by the painters of the twelfth century." Evidently castor oil must have been heated before such use. As is well-known, during heat treatment the ricinoleic acid of castor oil decomposes into water and one of two linoleic acids :—

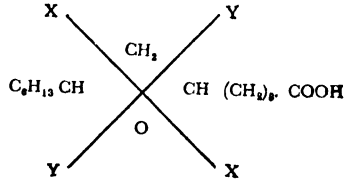
1. $CH_3.(CH_2)_4\ CH{-}CH\ CH_2\ CH{=}CH\ (CH_2)_7\ COOH$
   Δ 9, 12 linoleic acid

2. $CH_3.(CH_2)_5\ CH{=}CH\ CH{=}CH\ (CH_2)_7\ COOH$
   Δ 9, 11 linoleic acid

Although Schieber claimed that the resultant fatty acid mixture consisted of nearly 90 per cent. of the conjugated acid, this claim has not been substantiated and it has been found that not more than one-third of the ricinoleic acid changes to 9 11 linoleic acid. The dehydrated castor oil films have excellent colour retention properties Side by side with the formation of dehydrated castor oil, decomposition of the oil takes place to some extent. Barbot[11] carried out an extensive investigation into the behaviour of castor oil on heating. He came to the conclusion that the reactions taking place can be divided into two classes, A and B

A Decomposition into water and a drying oil with the loss of the hydroxyl group in the ricinoleic acid chain as described above.

B. Decomposition into other products, including heptaldehyde, undecenoic acid, octylene, sebacic acid semialdehyde, acrolein, myristic, palmitic, stearic and oleic acids To explain the formation of some of these compounds, Barbot postulated that ricinoleic acid exists in a tautomeric form ·



Fission along the line XX would give

$C_6H_{13}.CHO$	and	$CH_2=CH.(CH_2)_8.COOH$
n-heptaldehyde		10, 11 undecenoic acid

while fission along the line YY would yield

$C_6H_{13}CH=CH_2$	and	$CHO\ (CH_2)_8\ COOH$
Octylene		Sebacic acid semialdehyde

Evolution of water begins at 185-190°C., the rate increasing with rise of temperature. The decomposition B does not commence until a higher temperature is reached, the rate becoming appreciable at 285-290°C. The chief products are heptaldehyde and undecenoic acid and at higher temperatures the yield of these is greatly increased. To reduce these decompositions to the minimum it is therefore necessary to keep the temperature below 280°C, and since the rate of dehydration is slow at this temperature, to use a catalyst Various catalysts have been used for this purpose Sulphuric and phosphoric acids and their acid salts have been used with success Other catalysts are oxides of such metals as aluminium, zinc, tungsten ; persulphates, sulphonic acids, etheionic acid , chlorides of iron, zinc, calcium, silicon, phosphorus, etc Kappelmeier and his collaborators[12] have found however that the degree of decrease in hydroxyl value cannot be taken as the true criterion of the extent of dehydration of castor oil, as ester-interchange between the glyceride and the secondary alcoholic group of ricinoleic acid takes place simultaneously with dehydration As a result the dehydrated oil contains protected hydroxyl groups whose presence is revealed by determining the hydroxyl value of the methyl esters of the fatty acids obtained from complete saponification of the oil.

When castor oil soap is heated in presence of alkali, secondary octyl alcohol (2-octanol) is distilled off and sodium sebacate remains behind :

$$\text{Castor oil} \xrightarrow[\text{heat}]{\text{NaOH}} CH_3.(CH_2)_5.CHOH.CH_3 + NaOOC.(CH_2)_6.COONa + H_2$$

Sebacic acid can be obtained from the residue by extraction of the latter with hot water and subsequent acidification of the aqueous liquid, when the acid separates in the form of white laminae. A study of the maximum production of sebacic acid from castor oil soap was carried out by Verma and Aggarwal[13] ; they found that the maximum

yield of this acid obtained when castor oil soap is heated gradually to 200°C. in the presence of 20-30 per cent. of caustic soda. The yield of secondary octyl alcohol is however maximum when the soap is heated with 30 per cent sodium carbonate If the soap and alkali mixture is heated under a pressure of 700 lb per square inch and at 260°C. an yield as high as 53 per cent of sebacic acid is obtained. Sebacic acid is an important raw material in the manufacture of long-chain polymers and alkyd resins, and is also a starting material for the synthesis of muscone Secondary octyl alcohol when esterified with sebacic acid or phthalic acid gives valuable plasticizers. Octyl phenate is a very good fungicide and germicide.

On heating the dehydrated castor oil further it is transformed mostly into an insoluble material of brownish-yellow colour known as castor oil gel. No industrial uses exist for this material and if through lack of proper precautions during the manufacture of dehydrated castor oil the gel is obtained, it represents that much net loss. Ranganthan and Siddiqui[11] have, however, developed a process for converting the gel into a soluble viscous liquid which may be used for the manufacture of varnishes, enamels, paints, adhesives, waterproofing composition and like materials. Their process mostly consisted of gradual heating of the gel under carefully-controlled conditions up to 275°C. till the entire gel was transformed into a thick viscous liquid. Gupta, Verma, Aggarwal and Siddiqui[15] carried out the chemical analysis of this viscous material and found it to be a mixture of derivatives of dicarboxylic and mono-carboxylic acids of unsaturated character, which might have been derived from cracked and uncracked products of monomeric, dimeric and also polymeric linoleic acid glycerides. The liquid also consisted of 7 to 8 per cent. of unsaponifiable matter composed mainly of aldehydes and hydrocarbons.

Castor oil gel has, however, been transformed in almost quantitative yield into a yellow viscous liquid product by Aggarwal and Gupta[16] by heating it in presence of steam under pressure. The product has also a much lighter colour than the one produced by the method of Ranganathan and Siddiqui. Besides the uses mentioned above, the polyvalent metallic salts of the acids from the liquid product, when treated with linseed oil, give oil varnishes whose films are quite resistant to water and electricity and have very high gloss. A complete analysis of castor oil gel has recently been made by Bhasin and Aggarwal[17]. The gel has been found to contain about 40 per cent. of material

which dissolves in mixtures of ordinary organic solvents while the rest is absolutely insoluble and infusible. The soluble portion consists of 75 per cent. of dimerised linoleic acid and 25 per cent. of a monomeric product whereas the insoluble portion consists of 90 per cent. of the dimerised acids. The dimer acid portion of the insoluble part of the gel is most probably a mixture of di- and tri-carboxylic acids.

It is hoped that with the industrial progress of India, more and more uses will be found for this important raw material of which this country holds almost a monopoly.

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DISCUSSION

The following participated :—

Mr. H. H. Mathur, National Chemical Laboratory, Poona.

Prof. B. N. Banerjee, Indian Institute of Science, Bangalore

Dr. B. S. Kulkarni, Department of Applied Chemistry, Osmania University, Hyderabad-Deccan.

Dr. S. H Zaheer, Central Laboratories, Hyderabad-Deccan

Dr. S. A. Saletore (President), Central Laboratories, Hyderabad-Deccan.

Dr. M. G. Krishna, Central Laboratories, Hyderabad-Deccan.

Dr. G. S. Sidhu, Central Laboratories, Hyderabad-Deccan.

Dr. K. T. Achaya, Central Laboratories, Hyderabad-Deccan

Mr. N. Bhojraj Naidu, Central Laboratories, Hyderabad-Deccan.

Mr. M. A. Sivasamban, Central Laboratories, Hyderabad-Deccan.

Mr. Bharat Bhushan, Central Laboratories, Hyderabad-Deccan

Since *the gel* produced from dehydrated castor oil appeared to have *few uses*, several enquiries were made regarding an anti-oxidant for the latter product (B.N.B.) and as to whether it was not advisable to utilize the oil before it gelled (M.A S.). The speaker (J.S A.) said that while this was indeed so, gel formation often occurred and this paper merely considered uses for such a gel. In reply to a query (M.A.S.) he stated that the products obtained on de-gelling and re-heating were usually fission products from various gel components

Much attention was directed to the actual dehydration of castor oil, and several aspects of this problem were brought up for discussion Since it was *ricinoleic acid* which gave castor oil its distinctive properties, it was suggested (N.B.N.) that the acid *should be segregated* and then utilized, for example for the manufacture of aeroplane dopes, while it was also being used in tooth pastes as its sodium salt (K.T.A.). The speaker (J S.A.) however was of opinion that though Schieber had originally used ricinoleic acid for dehydration, this was both uneconomical and difficult, owing to the tendency of the latter to polymerise, though it no doubt yielded a large proportion of conjugated acids than whole castor oil. It was suggested that the proper approach would be segregation of the large porportion, about 70 per cent., of triricinolein occurring in castor oil, and that solvent-extraction methods had been

used successfully on a small scale for this purpose (K.T.A.). The unsatisfactory nature of knowledge regarding the composition of castor oil (*e.g*, the literature stated that its oleic acid content varied from traces to 10 per cent.) and of its dehydrated product was commented upon (K.T.A.), and emphasised by the President (S.A.S.). In response to an enquiry (G.S.S.), the speaker (J.S.A.) said that the intensive hydrogenation of ricinoleic acid yielded stearic acid

The feasibility of the Barbot mechanism for dehydration mentioned by the lecturer was doubted, one speaker (G.S.S.) remarked that the propylene oxide ring is very stable and on scission would yield nonaldehyde and heptoic acid; another (B.B.) said that, on the analogy of the terpenes, scission of the propylene oxide ring would occur at a point away from the carboxyl group. It was pointed out that the ring was probably only existent as a momentary phase (H.H.M.)

The unsatisfactory nature of the methods used for following the progress of dehydration was discussed in some detail. Acetyl values were stated to be of little value (M.A.S.), one suggested reason being the interaction of hydroxyl groups at high temperatures, since even at ordinary temperatures an increase in viscosity and a rise in apparent acetyl value of castor oil is observed (K.T.A.). The President (S.A.S.) thought that solubility in alcohol and in petrol ether, and changes in refractive index, could be used to follow the course of dehydration, though the speaker (J.S.A.) remarked that since both dehydration and polymerisation affect these criteria, a film-drying test, though slow, was probably best. The lack of published details regarding the process were also remarked on by the President and the speaker.

Several enquiries were made (M.G.K., B.S.K.) about the actual *comparative drying qualities* of dehydrated castor oil. The speaker (J.S.A.) answered that in general the product is quicker-drying than linseed owing to its content of conjugated acids. The colour of the product was of course dependent upon the catalyst, contact with air, temperature, etc., and a dark colour was objectionable from practical considerations, whether this was related to drying power or not (N.B.N.).

Enquiries were made (G.S.S.) regarding the *toxic principle of castor seed*, ricin; it was stated to be destroyed by heat, and was not present in hot-pressed oil (H.M.M.). [It may be remarked that three toxic principles are known to exist: first and mainly, a protein, ricin, denatured and detoxified by heat; secondly, an allergenic material of

protein-polysaccharide nature ; and thirdly, a mildly toxic alkaloid, ricinine.—Ed.].

What contributed to the laxative quality of castor oil (G.S.S.) ? It was believed not to be ricinolein (N B N) ; a sample of oil stated to have been prepared by a French patent and to be " edible " was found on analysis to correspond exactly with castor oil (S H Z.). The speaker (J.S A.) added that it was largely a question of degree, since all oils possess this property to some extent ; *e.g.*, olive oil, normally considered edible, was laxative when consumed in large amounts. [Apart from whole castor oil, pure ricinoleic acid and its glycerides have been shown to have cathartic properties, acting either on the intestinal mucosa or on the Auerbach plexus — Ed.]

A number of incidental questions were raised . the *transparency of soaps* containing castor oil was recommended for study (N.B.N) ; *lipase* from castor seeds could be used as an economical means of *fat splitting* (B.N.B.) ; the use of high-pressure steam (at about 1500 atmospheres) for fat splitting (B N.B.) was considered neither feasible in India nor likely to replace the simpler and cheaper methods now used here (S.A S., J S.A.).

UTILIZATION OF TOBACCO SEED, SAFFLOWER AND LIKE OILS AS SURFACE-COATING MATERIALS

by

DR. J. S. AGGARWAL

(*National Chemical Laboratory, Poona*)

Linseed oil is the drying oil commonly used in India in coating compositions. Although formulations containing this oil give hard and glossy films these become yellow after some time. To overcome this defect, dehydrated castor oil, either in admixture with linseed oil or alone, is used for coating compositions. To further supplement the amount of these drying oils it is necessary to find some other cheaper materials whose availability may be in appreciably large quantities. Fortunately India is quite rich in oils which contain linoleic acid as a major component fatty acid. Some of these oils available in India are —

Oil	*Approximate linoleic acid content (per cent.)*
Tobacco seed ..	54-75
Safflower seed ..	51-78
Poppy seed	62-65
Argemone .	48-62
Niger seed ..	53-72
Sunflower seed ..	52-66
Melon seed ..	45
Water-melon seed ..	48-49
Cotton seed ..	41-54

Of these, tobacco seed, safflower, Niger seed, cotton seed and poppy seed oils are quite easily available in this country. Thus 8000 tons of tobacco seeds are available in Madras province alone, and these yield on an average 25 to 40 per cent. of a greenish-yellow, odourless oil. Cottonseed is mostly obtained in Bombay, the Punjab, Madhya Pradesh and Hyderabad, with a total production of 21,28,000 tons annually. Indian poppy is mostly cultivated in Uttar Pradesh and in the

Rajputana States. Niger seeds are grown in Chota Nagpur (Madhya Pradesh) and the Deccan, while the chief areas for the crop of safflower seeds are Madhya Pradesh and the Southern Mahratta country.

With such a big production of such oilseeds in this country it is necessary to find methods for the conversion of these oils into modified products which can be used in coating industry either alone or in admixture with linseed oil. This would to a great extent relieve the great demand for linseed oil and incidentally the product might be free from the defects which are inherent in linseed oil, particularly yellowing of the film Narsimha Rao and Ramanayya[1] produced double-boiled tobacco seed oil by heating the raw oil in iron kettles over a direct fire at 220 to 240°C for 8-9 hours, and found the product to be inferior to double-boiled linseed oil made in the same way. They found that the film of this oil got tacky after a few days, though the film was more lustrous and flexible than linseed oil film.

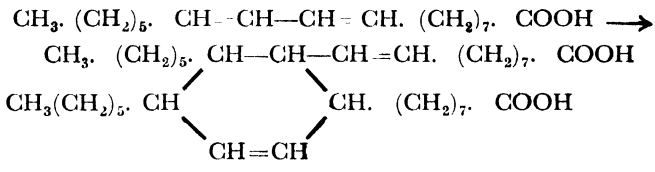
Blown oil from tobacco seed oil was made by heating the oil with closed steam coils at 130-150°C. and blowing compressed air for about 15 hours, adding the usual chemicals, and blowing again for 10 hours. Blown tobacco seed oil resembles blown linseed oil in several respects, but differs from it in having a lower specific gravity, greater flexibility and decreased lustre of the film. When mixed with certain proportions of linseed oil good paint oil can be obtained.

Tobacco seed oil was also polymerised for about 20 hours in iron kettles at 260-280°C. The product obtained closely resembles polymerised linseed oil, the only difference being its lower specific gravity. The oil was employed in long and short rosin varnishes when good products were obtained, the film being more flexible and less brittle than that of linseed oil-rosin varnishes. Poinot[2] reports the result of his experiments on the use of tobacco seed oil in the production of paints and varnishes. A great similarity with linseed oil was observed and the difference in drying was very slight. Rowaan[3] also finds tobacco seed oil satisfactory for the preparation of special paints

Saletore and Shrivastav[4] found safflower oil suitable for oilcloth manufacture, giving a film of very good flexibility and abrasion resistance. In mixture with dehydrated castor oil it has been specially recommended for this purpose. Safflower oil has been regarded as a potential oil crop for paint manufacture in Australia[5] and its mixtures

with soyabean and linseed oil have also been recommended[6] as efficient coating materials. Stand oil has also been prepared from sunflower seed oil[7]. Extensive research work has been undertaken in the National Chemical Laboratory of India on the modification of tobacco seed and safflower oils so that their films would dry quite rapidly and they could then be used in paints and varnishes. It has been found that these oils when treated with a very small amount of resorcinol dry in four and a half hour. Isomerisation of these oils in presence of substances like specially prepared nickel-carbon, anthraquinone, benzoquinone and naphthaquinone on the lines suggested by Falkenburg and others[8], and by Radlove, Teeter, Bond, Cowan and Kass[9], gave products of very pale colour whose films dried in 3½ to 4½ hours They retained their original colour and never became yellow on aging as is the case with linseed oil films The ester gum varnishes of these modified oils gave smooth glossy films which were quite resistant to water The titanium dioxide paint film remained absolutely white and bright even after six months. The interpolymerisation of these oils with other substances give products which are quick drying and whose films are quite elastic and colourless.

Bradley[10] found that if the methyl ester of linoleic acid is heated at high temperatures for 8 to 20 hours, two molecules of the acid combine by a Diels-Alder reaction to form the esters of dilinoleic acid ; thus, for the acids ·



Bradley showed that the heat bodying of such linoleic acid-rich and other highly unsaturated oils occurs largely through a dimerisation reaction similar to the one illustrated above. As a matter of fact, by the heat polymerisation of dehydrated castor oil and some other linoleic acid-rich oils, he and his collaborators could isolate dimer acids along with monomeric fractions. The constitution of these dimers, and the chemical reactions involved during the heat-bodying of these oils with ultimate gel formation, have been a subject of controversy between him, Sunderland, Farmer and Bernstein. The actual structural formula for the dimerised acid has been proved by Petit[11] and

Champetier and Petit[12] who established the cyclohexenic or hydroaromatic nature of the dimeric acid. The dimer acid is a liquid, dibasic acid, viscous in nature, with an apparent molecular weight of approximately 600. Its volatility is low, heat stability excellent and oxidation resistance high. It undergoes reactions typical of this class of compounds and many uses are based on its dibasic character Thus with ethylene diamine it forms resins which have shown possibilities as coating materials. With high diamines it forms long chain polyamides When this acid is substituted in part for phthalic anhydride in the production of alkyd resins, the products formed give films with superior durability and flexibility to the one produced by phthalic anhydride alone. Since the formation of a dimer is probably the first step in the subsurface drying of an oil, the value of modifying such an oil by incorporating a preformed dimer is a logical inference. It has been found that when a dimer acid and drying or semi-drying oils, or their fatty acids, are esterified with glycerine or other polyhydric alcohols, bodying time is reduced and the control of viscosity is simplified. The dimer acid has also formed an ingredient in varnish formulations. The other uses of dimer acids are in the formulation of plasticizers, long chain polyesters with rubber-like characteristics, lubricant additives for improving the viscosity index and pour point, adhesives, greases, hot tin dipping baths, textile assistants, insecticides and emulsion breakers. The divalent and polyvalent salts of the dimer acid and other polymerised vegetable oil acids have been found to give drying oil varnishes whose films have excellent gloss, and water-solvent and electric-resistant properties It has also been found that if small amounts of the mercury or copper salts of these acids be used in paints, the films are saved from fungus and mould attack.

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(*Sunday 13th August* 1950).

DISCUSSION.

The following participated :—

Dr.-Ing. H. G. Kayser, Laxminarayana Institute of Technology, Nagpur.

Dr. B. S. Kulkarni, Department of Applied Chemistry, Osmania University, Hyderabad-Dn

Dr. S. A. Saletore (President), Central Laboratories, Hyderabad-Dn

Dr. M G. Krishna, Central Laboratories, Hyderabad-Dn.

Dr. P. M Bhargava, Central Laboratories, Hyderabad-Dn.

Mr. Bharat Bhushan, Central Laboratories, Hyderabad-Dn.

The picture of the *changes occurring as a result of blowing* were much more complicated than had appeared from the speaker's account, the President (S.A.S.) said ; not only were acids involved, but glycerides containing three not always similar acids. Several types of changes were possible — intermolecular and intramolecular to give large molecules, breakdown reactions to yield fragments which could conceivably react further.

Moreover, *the analytical methods available were not so delicate or so precise* as to follow all the changes completely (S.A.S.). The speaker (J.S.A.) described the methods used for the separation of polymers . either molecular distillation or solvent segregation was employed ;

in his own laboratories, the polymerized material was taken up in a mixture of acetone and methanol (1 ; 1) when separation occurred of the very high molecular weight compounds ; if no separation was obtained more methanol was added (and in some cases water) to yield a fractional separation. The President (S.A.S.) considered that any method involving alkali saponification was rather drastic, and would at best throw light on the acidic part, and not on the whole of the molecule. More feasible methods would be those involving molecular distillation, chromatography, and X-ray or other physical measurements.

Would not eight-membered rather than six-membered rings,as described by the speaker, be produced by *condensation of two linoleic molecules* (B.B.) ? Again, would not isomers be formed as a result of the condensations described (P.M.B.) ? The speaker (J.S.A.) replied to say that actually 1 : 2, 1 4 addition (to yield six-membered rings), rather than 1 : 4, 1 .4 addition (yielding eight-membered rings), appeared to be in preponderance. Of course isomers of different types—positional, optical, etc.,—are all possible and probably do exist.

The economics, edibility and utilisation of tobacco seed and safflower oils were the subject of some discussion. The comparative prices and availabilities of the two oils, and their ability to compete with linseed, were enquired of (H.G.K., M.G.K.). The speaker (J.S.A.) replied to say that tobacco seed oil was just a waste product today and its utilization would probably bring down the cost of tobacco itself. In reply to a query (B.S.K.), he stated that while he had not himself worked on the subject, reports from other sources and countries had indicated that tobacco seed oil was indeed edible. Speaking about safflower oil, it was an edible oil in India and, considering the shortage of the latter, was not likely to be available for use in paints. Both oils could certainly compete with linseed in regard to serviceability in paints. The President (S.A.S.) said that no doubt new oils would continue to be found to meet special needs, such as for use in artists' paints, where linseed oil caused eventual yellowing and was therefore objectionable , there was also a need for more satisfactory resins than those at present available and the oils today described could perhaps be of value for this purpose.

NUTRITION

by

PROF B. N. BANERJEE

(*Indian Institute of Science, Bangalore*).

In considering nutrition with respect to fats, one has to consider two factors :— the glyceride portion and the unsaponifiable matter. From the physico-physiological point of view, three subjects merit consideration : the digestion and absorption of fats, the storage property of fats, and the solvent action of fats on vitamins and carotene. I shall deal today only with the latter two aspects, which in a sense only indirectly concern nutrition, and omit the digestibility and absorption of fats, as some discussion on this subject has already occurred earlier in this symposium.

In studies on proteins, by common convention, casein has been taken as a standard or norm ; for carbohydrates, glucose has been used as a reference for comparative standard purposes. Why not use butterfat as a standard for fats in nutritional work ? What should then be the qualities and properties of such butterfat, which should obviously be of high, but standard, quality ?

(*a*) *Free fatty acids.*—This may range in the natural product from nothing to almost anything. To obtain a minimum acidity in ghee it is necessary to use freshly-drawn milk of very low acidity (0.09-0.10 per cent. lactic acidity), to separate the cream immediately, to prepare butter by churning and butterfat by decantation. In any case, it was found impossible to go below 0 02 per cent. free fatty acidity (as oleic) and this figure will probably have perforce to be our standard. For vegetable oils also, similar extraction methods using fresh, healthy seed gave oils which did not fall below 0 02 per cent. acidity (as oleic). But again the question arises—is free fatty acidity the only criterion of quality and storage property of ghee ? What other factors are of importance ?

(*b*) *The composition of the fat* is clearly of great importance for this. Fats are mixtures of glycerides of various fatty acids (lower and higher,

saturated and unsaturated) existing moreover in various forms (symmetrical, unsymmetrical, polymorphic, cis, trans, etc.). Different crystalline physical structures, and hence melting points and X-ray spacings, are possible for the same fat, and such changes can take place in the ordinary operations that oils and fats are subject to. During hydrogenation, for example, iso-oleic acid is formed and has a higher melting point than oleic, and other unusual properties ; with unsaturated acids especially such changes are highly complex and do occur. From its fatty acid structure it has been computed that ghee can give rise to some 22,848 compounds. Clearly then it would be almost impossible to correlate changes in chemical (glyceride) composition of ghee with any difference in its storage property or quality.

(*c*) We have however *practical methods of studying* the overall effect of these factors by observing the storage qualities and especially the concomitant destruction of vitamin A and carotene when fat is used as a solvent carrier The usual method of study of storage property is by accelerated oxygen tests, using the length of the induction period, usually at elevated temperatures, as the criterion of ability to keep. Various tests like the peroxide value, Kreis test, iodine value, thiocyanogen value, etc., can also be used for this purpose, especially under comparative conditions.

(*d*) By such tests it was found that *the quality of seeds*—whether broken, or shrivelled, or mouldy, or whole—affects markedly the oil produced from them and, of course, no laws exist to control either seed gradation or oil quality. Even the colour of the seed appears in some cases to be of importance : for example, using sesame oil, white seed gave oil of low acidity while black seed yielded oil of higher acidity. In the case of coconut oil, fresh copra extracted by the Cochin process gave oil of very low acidity (0 02-0 05 per cent.), while market copra gave oils of acidities 1 5-3 0 per cent , on sun-drying of copra this was raised to 3 5-4.5 per cent., while oven-dried copra gave oils of about 2 per cent. acidity Steaming the meal for extraction increased the acidity double-fold. Of course the other values, like peroxide value, were different under these conditions. It is however abundantly clear that oil of very low acidity can be obtained in India by proper gradation of seed and correct storage processes. Refined oil of low acidity is never as good as fresh oil of the same acidity, and an antioxidant gives better protection with a fresh oil than with a refined oil. It would appear as

if certain irreversible molecular changes have occurred in the oil during rancidification.

It is valuable to analyse the role of various substances in the phenomenon of rancidification of an oil or of prevention of such rancidification, paying attention particularly to the non-fatty matter, which is somewhat more amenable to study than the glyceride though complex enough in itself ; it consists generally of sterols, hydrocarbons, tocopherols, lecithin, colouring matters, vitamins A and D, etc.

The tocopherols were found to have antioxidant properties , the contents of tocopherols in various oils and hydrogenated oils were studied (by the Emmerie-Engel method) and it was found that the loss during refining and hydrogenation was not high, being about twenty per cent. Tocopherols protect not only the fat but also the highly-unsaturated carotene from oxidation, and this latter in turn is found to be an antioxidant in itself. Refining methods should aim as far as possible at preserving natural antioxidants ; usually much of these are destroyed and pro-oxidant bodies are formed, which again might partly explain the lower storage properties of refined oils. The addition, compulsory by law, of small quantities (5 per cent.) of sesame oil to hydrogenated fats was found (using two products of melting points 37°C. and 41°C. respectively) actually to effect marked improvement in the storage properties of the fats, probably owing to the protective action of the tocopherol or sesamol of the sesame oil.

Degradation changes of much interest take place in the unsaponifiable constituents of oils during the development of rancidity. Grossly, the digestibility and storage property of the oils are lowered. The tocopherol and sterol contents are lowered, while curiously, the melting point of the sterol acetate is also lowered. The proportions of the alcohol-insoluble portion, relative to the alcohol-soluble portion of the total unsaponifiable matter, is increased during rancidification. Evidence has been obtained indicating that the hydrocarbons (alcohol insoluble) produced by the breakdown of sterols during spoilage are unsaturated and pro-oxidant. This may be another way in which the results of refining accelerate the oxidation of oils.

The products of rancidity, measured by such tests as the peroxide value, Kreis test, free fatty acidity, etc., which are increased in different proportions according to the conditions, cause greatly-increased destruction of the vitamin A or carotene for which they act as carriers or

solvents. U.P. Basu has reported that soon after the addition of a vitamin A concentrate to natural glycerides or to esters, an initial loss occurs which may be prevented by the addition of an antioxidant. But this has to be added to the substrate in the first instance, before addition of the vitamin concentrate, if it is to have any effect, otherwise the initial rapid vitamin loss due to peroxide bodies cannot be prevented ; the antioxidant appears to prevent the peroxide bodies from oxidising the vitamin A Similarly a substance like oleic acid is not by itself an antioxidant but acts as a synergistic agent for the antioxidant in an ester or glyceride system The destruction of vitamin A in oils during normal cooking (frying) processes was found to be very great when the oil was highly acid , lowered acidities of oil markedly reduced vitamin destruction during frying

Finally, edible oils like coconut, groundnut, sesame, etc , from healthy seeds, with acidities of upto 1 per cent (as oleic) are perfectly satisfactory from the point of view of digestion and absorption, storage property (if antioxidants are used) and as solvents or carriers for vitamin A and carotene Up to about 2 per cent free acidity, these oils may be tolerated for edible purposes, but beyond this figure they should only be used for industrial purposes. The refining of rancid or highly acid oil improves it somewhat by removing undesirable matter, but refining cannot restore the natural properties of a good raw oil.

(*Monday* 14*th August* 1950)

DISCUSSION

The following participated .—

Dr. J. S. Aggarwal, National Chemical Laboratory, Poona.

Mr. H. H. Mathur, National Chemical Laboratory, Poona

Mr. G. V. Ramaswami, Vegetable Oil Factory, Mettur.

Dr. S. A. Saletore (President), Central Laboratories, Hyderabad-Deccan.

Dr. G. S. Sidhu, Central Laboratories, Hyderabad-Deccan.

Dr. K. T. Achaya, Central Laboratories, Hyderabad-Deccan.

Mr. Bharat Bhushan, Central Laboratories, Hyderabad-Deccan.

Mr. Baldev Singh, Central Laboratories, Hyderabad-Deccan.

An *ideal fat* for use as a standard or norm had been mentioned by the speaker, and it was suggested (G S.S.) that a synthetic fat might meet the requirements In the speaker's (B.N.B.) view, however, a synthetic fat would hardly include all the factors likely to be involved in any study of fat problems.

Hydrocarbons had been mentioned by the speaker *as being pro-oxidants*, which certainly appeared very surprising (J.S.A.) ; it was pointed out however, that work since about 1920 had shown that hydrocarbons are not as inert as generally believed and that even saturated hydrocarbons can be transformed by simple air-blowing into alcohols, etc., though of course in very small quantities (B.B.) it was entirely possible that these breakdown products could act as pro-oxidants in fats The speaker (B N B) again confirmed his original observation that the alcohol-insoluble portion of the sterol fraction was found to increase in relative proportion during rancidification and to function as a pro-oxidant. Of course the glyceridic fraction also altered during storage ; it had been found experimentally that refined oil to which the unsaponifiable matter from fresh oil had been added was not as stable as fresh oil.

Synergists and anti-oxidants in vegetable oils were next discussed. It was emphasised that oleic acid was not an antioxidant but merely a synergist and that these two functions were apparently not related (J.S A) , the case of sesame oil was quoted to illustrate the point that only certain fractions of the unsaponfiable matter could function as antioxidants, since removal of sesamin was found by the speaker not to affect the stability of the residual oil (B S). It was pointed out however that the antioxidant of sesame oil was neither sesamin nor sesamolin but sesamol, so that removal of the former would hardly result in any loss of stability (H.H.M)

Though *the digestibility of fats* had not been included in the paper presented, it was alluded to by several speakers. Enquiries were made regarding the superiorities variously claimed for unsaturated oils, for fats containing lower fatty acids, and for fats of low melting point (J S.A.) ; it was pointed out that while total digestibilities below a melting point of 45°C. were generally of the same order, it was believed that the time of digestion was less for fats containing the lower fatty acids and that this reduced the calcium-phosphorus ratio to an economic level (K.T.A.). The speaker (B.N.B.) cautioned that there was no

doubt much truth in every theory, since individual variations, such as in degree of emulsification of fat or in bile salt availability, were enormous ; long-term experiments would be essential to decide the question (G S S) ; moreover, human depot fats contained almost only palmitic and oleic acids, and were other fatty acids really needed (G V R), beyond of course the essential, so-called " vitamin " acids, linoleic, linolenic and arachidonic (B.N.B.) ? The President (S.A.S.) enquired if free fatty acids aided digestion in any way ; the speaker (B.N B) replied that the effect was clouded by so many other factors that it was difficult to say for certain, though high degrees of acidity were commonly supposed to be harmful.

RANCIDITY OF VEGETABLE OILS

(with reference to the part played by non-glyceridic components and atmospheric nitrogen)

by

DR. S. A. SALETORE

(Central Laboratories, Hyderabad-Dn.)

Though over two hundred papers have been published on the subject of rancidity, most of them have dealt with tests for evaluation of rancidity or with the effect of various factors such as heat and light on same, and a goodly number have been devoted to various methods of retarding rancidity by the use of natural or synthetic inhibitols and antioxidants ; but the fundamental nature and mechanism of rancidity has been tackled by only a few workers and to this day is still to a great extent a mystery. That rancidity in some cases is caused by bacterial action is known, and it has also been shown that enzymes can and do give rise to rancidity, but possibly the worst criminal responsible for spoilage of oils and fats is atmospheric oxygen. A great deal of thought and effort has been expended on unravelling this attack of atmospheric oxygen on oils and fats, and the general opinion that now holds the field is that this action of oxygen takes place at or near the unsaturated carbon linkages, and that once started it proceeds as an autocatalytic reaction.

As to how this oxygen combines with the unsaturated oils has been a matter of perennial interest during the last fifty years and a fruitful field for speculation. Of the various theories proposed, Fokin's(1) ethylenic theory, propounded in 1909, generally held the field till 1925, when Staudinger (2) put forward his theory of autoxidation based on the formation of peroxides, and till recently this was accepted by most scientists. The hydroperoxide theory of Farmer and his co-workers (3) has now taken its place, supported as it is by a considerable amount of evidence, and this is finding increasing support in the work of other poeple. In this connection it is interesting to read Markley's comments(4) :—

> " A vast literature has appeared on the subject but as yet no clear understanding of the complete reaction mechanism involved has appeared. Many theories have been advanced and much experimental evidence has been accumulated to substantiate one or another hypothesis. Some of the theories and experimental evidence have resulted in confusing rather than clarifying the problem, but gradually there has been adduced a few fundamental principles which will eventually lead to a complete understanding of these mechanisms."

Having accepted the fundamental theory that rancidity is due to a great extent to reaction of atmospheric oxygen with unsaturated oils and fats, it is not surprising that most of the methods devised by workers in this field for studying the progress of this type of rancidity should be based on the chemical reactions of oxidation products.

One of the earliest of such tests is the well-known Kreis test (5) which is stated to be due to the reaction of aldehydes, formed as a result of oxidation of the oil or fat at the double bond, with an ethereal solution of phloroglucinol. But though subsequent workers (6) have tried to make this test quantitative, it is doubtful if the Kreis test is entirely satisfactory for purposes of evaluating rancidity. Lea's peroxide value (7) in its improved modifications is probably the most popular test now employed by workers as an index of rancidity. The peroxide value, as the word itself indicates, depends on the existence of peroxides, which again are stated to be formed by the linking of atmospheric oxygen with the unsaturated centres of the oil or fat. Besides these two, a number of other tests have been devised, all of them based on the phenomenon of absorption of oxygen by the unsaturated oil The main point to notice in all these rancidity studies is that it has been taken for granted, fundamentally, that rancidity is due to atmospheric oxygen combining with the unsaturated linkages.

While thus on the one hand we have had a series of excellent theories purporting to explain the nature and mechanism of rancidity, and chemical tests for the study and evaluation of this phenomenon, on the other hand we are faced with certain facts which are definitely disquieting. If there is one characteristic which definitely differentiates a rancid oil from a non-rancid oil, it is its well-known peculiarly disagreeable smell. The nose is no doubt a very uncertain instrument

for evaluating smells, but a strongly rancid smell can neither be missed nor forgotten by any normal human being. Yet the fact remains that the organic chemist has not been able to attribute with any degree of certainty the smell of rancidity to any particular compound or mixture of compounds. Neither has he been able to explain satisfactorily the chemical reactions by which a sweet-smelling oil on exposure to air gives rise to the disagreeably smelling product of rancidity in course of time. If we were to go through the scientific literature looking for an explanation for the smell developed with rancidity, we would be left with the theories of Scala (8) and Powick (9) who attribute rancid flavours to the presence of heptylic and nonoic aldehydes and with Lea's idea (10) that rancidity is due to a mixture of lower fatty acids.

Except for these few specific references to organoleptic rancidity, the generality of modern scientific workers have been content to accept organoleptic rancidity as being due to breakdown products of the primary products of oxidation, namely, the peroxides or hydroperoxides. At the same time there does appear to be an uncertain feeling that none of the theories propounded so far properly explains the smell of rancidity.

If such is the position with regard to the theoretical aspect of the matter, it is no better when we come to the practical evaluation of rancidity. None of the tests so far devised can be relied upon absolutely, for while all rancid oils respond to the Kreis test and show peroxide values, the reverse is not always true. A positive Kreis test does not necessarily mean that the oil will smell rancid nor is there a minimum peroxide value for all oils indicating organoleptic rancidity. The statement attributed to Coe (11) that the organoleptic test is the only one of any value, taken in this context, is therefore significant.

What rancidity is, therefore, continues to be not fully or clearly understood. Much of the confusion that exists is due to the lack of a proper appreciation of the complicated nature of the problem, to too-ready an acceptance of oxidation as the root-cause of rancidity, and to some extent to the unsatisfactory nature of the technique followed. Thus, for example, a good deal of the work has been done on the methyl or ethyl esters of the fatty acids which are not true-to-life since they do not have the complex glyceride structure present in natural oils. Then again, rancidity experiments carried out on natural oils suffer from the defect that these tests are not done on the pure natural glycerides

but on oils containing a variety of non-glyceridic components, each of which may and very often does have some action on the course of the reaction, thereby detracting from the value of the results by bringing too many unknown factors into play The accelerated tests now largely employed (like the Swift stability test(12) carried out at an elevated temperature, or other tests carried out under some other artificial conditions), while they may be useful for comparative purposes, are apt to be misleading when applied to the development of rancidity under natural conditions.

The better stability displayed by natural vegetable oils compared to similar synthetic glycerides has been ascribed to the presence in the former of the so-called antioxidants But what these antioxidants are and how they behave does not seem perfectly understood as yet and conflicting opinions on the matter have been expressed. Olcott and Mattill(13) are of the opinion that the antioxidant activity is due to the tocopherols, while according to Hilditch and his co-workers antioxidants are similar to carbohydrates in nature(14). Carotene, a common constituent of oils, has been reported by some as having antioxidant properties and by others as being a pro-oxidant(15). To complicate matters further, in addition to anti- and pro-oxidants, oils are also supposed to contain synergists. Thus the picture we get of an apparently harmless-looking oil is that it is in reality an intensely-active battlefield, where antioxidants and pro-oxidants and synergists fight for dear life, till the inevitable happens and the oil molecule succumbs to the ravages of the air.

In order to undertand some of the factors that play a part in the development of rancidity, a series of experiments were carried out in Nagpur, first using fresh sesame oil of low peroxide value. Stability tests were carried out without recourse to either elevated temperatures or exposure to intense light, acceleration being obtained by the simple expedient of exposing a comparatively large area of the oil to air and diffused daylight in test-tubes each containing 0 5 gm. of the sample. The development of rancidity was followed by doing peroxide values on duplicate samples at regular intervals of time. Similar test runs were carried out on the filtered oil, oil freed of sesamin by means of acetic acid, and oil freed of sesamol as well by means of alcohol and subsequently treated with calcined alumina to remove any vitamins. The final sample was finally treated with bone charcoal. After a period of

41 days the oil samples had the following peroxide values :—

1. Fresh sesame oil	10
2. Filtered sesame oil	22
3. Sesamin-free sesame oil	11
4. Sesamin- and sesamol-free sesame oil	729
5. Oil No. 4 treated with calcined alumina	29
6. Oil No. 5 treated with bone charcoal	307

While the above experiments do support the theory that sesamol has antioxidant properties, it is difficult to explain why the sesamol-free oil should improve on treatment with calcined alumina, or show deterioration on subsequent treatment with bone charcoal.

Experiments were also carried out to see if the addition of small quantities of chlorophyll, β-carotene, the unsaponifiable matter from oils, and the extractive from the oil-cake had any effect on the development of rancidity in refined, bleached groundnut oil The results were disappointing, there being hardly any change in stability. In all these experiments with sesame and groundnut oil, a careful note was made of the stage at which the oil was organoleptically rancid. While in some experiments the oil developed the smell of rancidity at a comparatively low peroxide value (below 60), in other cases there was no bad smell even at as high a peroxide value as 175, indicating no particular relationship between peroxide value and rancidity by smell. As repeated experiments carried out at room temperatures under different conditions only continued to increase our doubts regarding the reliability of peroxide values for assessing rancidity in vegetable oils, we began to ask ourselves " Is it possible that in accepting oxidation as the root cause of rancidity we have overlooked some other parallel reaction which is taking place all the time ? If oxygen does not supply us with the key to the problem, what other common substance is there which we can regard as an alternative ? Since air consists mainly of oxygen and nitrogen, the question as it were forced itself on us could it be that nitrogen had something to do with the problem ?"

On the face of it this idea, to say the least, was preposterous, for nitrogen as we all know is a comparatively inert gas, and though it does react with other elements at high temperatures and pressures in the presence of catalysts, we have no evidence to show that it reacts

with organic compounds like vegetable oils under ordinary room conditions. But merely because the idea was unorthodox was no reason for abandoning it.

Recourse was then had to experiments and analysis to see if there was any kind of support forthcoming for this novel idea that atmospheric nitrogen takes part in the development of rancidity

This required accurate estimation of nitrogen in small quantities, and for this purpose the method devised by McGuire, Earle and Dutton (16) as modified by us has been found to be entirely satisfactory Employing this method, an analysis of three different samples of groundnut oil—one fresh, the other rancid and a third highly rancid—showed that while the fresh oil had 21 mgm of nitrogen per 100 gm of the oil, the rancid oil had 70 mgm and the highly rancid oil 129 mgm of nitrogen in it These results were encouraging but could not be taken as final proof of fixation of nitrogen, as vegetable oils are well-known to take with them mucilaginous protein matter from the parent seed during the process of extraction or expression, and though all three samples had been filtered through filter paper before analysis, it was just possible that the rancid oil samples may have taken into solution more of the mucilaginous protein matter, during extraction or storage, than the freshly-prepared oil.

An experiment was then carried out in which a batch of freshly-expressed, filtered groundnut oil was aerated by bubbling air through it, the flask containing the oil being kept on a water bath to accelerate the reaction. Samples were taken from time to time and examined for colour, peroxide value, and nitrogen content. The aeration experiment was repeated with another batch of oil and samples examined as before with the inclusion of iodine value determinations The results were striking. With the passage of air there was a steady rise in the nitrogen content and in the peroxide value, while the iodine value decreased. Fixation of nitrogen was definitely taking place.

In order to be absolutely sure that this fixation of nitrogen was not due to the presence of any bacteria or enzymes existing in the oil, a similar aeration experiment was carried out on the distilled ethyl esters of the mixed fatty acids of groundnut oil. The same phenomenon of a steady increase in the nitrogen content as a result of aeration was again noticed. In both cases organoleptic rancidity was noticed at a

certain stage, after which the oil smelled increasingly rancid. As the air used in the above aeration experiments was taken from the atmosphere existing in the laboratory, it was possible that it may have contained traces of ammonia or some other nitrogen-containing body or perhaps some bacteria. Subsequent experiments employing controlled quantities of air, carefully purified by passage through concentrated chromic acid solution, sulphuric acid, etc., have shown that these precautions have made no difference to the fixation of nitrogen by the vegetable oil. Similar experiments with linseed and coconut oils showed the same interesting phenomenon.

Now, whatever may be the root cause of organoleptic rancidity, there does not seem to be much doubt that we have discovered fixation of nitrogen by vegetable oils at atmospheric pressure and at a comparatively low temperature. This, in our opinion, is a discovery of a fundamental nature and of far-reaching importance.

What is the mechanism of this fixation of nitrogen; what are the catalysts, if any, taking part, is there any relation between this nitrogen fixation and oxidation, and what is the part played by nitrogen in the development of rancidity? These and several other questions crop up; without further experimental data it is not possible to give definite answers to any of them.

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(*Wednesday* 16*th August* 1950).

DISCUSSION

The following participated —

Dr J S Aggarwal, National Chemical Laboratory, Poona

Mr G. V. Ramaswami, Vegetable Oil Factory, Mettur

Dr K Ramachandran, Central Laboratories, Hyderabad-Deccan

Dr G. S. Sidhu, Central Laboratories, Hyderabad-Deccan.

Dr. K T. Achaya, Central Laboratories, Hyderabad-Deccan

Mr N. Bhojraj Naidu, Central Laboratories, Hyderabad-Deccan.

Mr Baldev Singh, Central Laboratories, Hyderabad-Deccan.

Mr. Bharat Bhushan, Central Laboratories, Hyderabad-Deccan.

The *new theory* of nitrogen-fixation by fats had a *deep significance* in that so far the phenomenon had only been realized in connection with bacteria (B. B) ; it would be of unusual interest to find out in what form the nitrogen was fixed.

In answer to various queries, the speaker (S.A.S.) gave details of the *work so far done.* Moisture had been rigidly excluded in one series of experiments and was not an influencing factor (B.B.) ; while particularly sterile air was not tried, some of the experiments were conducted at 95°C. at which temperature micro-organisms were hardly likely to exist (G.S.S) ; using linseed oil and pure nitrogen gas, the same phenomenon was observed, so that the accompanying oxygen of air was not essential for nitrogen fixation (G S S.) , using oxygen from cylinders, removal of accompanying nitrogen was very difficult, and further work is necessary (B.S).

Indeed much *further work* remained to be done, and various *suggestions* were put forward. Organoleptically rancid oils of low peroxide value could be examined for nitrogen content relative to bland oils of high peroxide value, to yield some clue to the mechanism of nitrogen fixation (G.V.R) It was pointed out that the highly-unsaturated oils, *e.g* linseed oil, had greater capacity for fixation (N.B.N.) , the material absorbed on the alumina column should have been examined, while experiments conducted in a dark room would be most revealing (G.S.S.). The role of the different constituents of an oil was also obviously of importance (G S.S), while isotopes of nitrogen would be ideal for study of the fixation mechanism (K.R.).

Regarding the earlier *oxidative work,* the highly pro-oxidant effect of bone charcoal may be due to its relatively large content of occluded oxygen , degassification of the charcoal should prove the point (K.T.A.). The different paths of oxidation at different temperatures, mentioned by the speaker, was supported with mention of the work of Gunstone and Hilditch ; a potent factor in the autoxidation of fats, often overlooked, was the injury of the fatty acids and glycerides during preparation (K.T.A.) The rancidity of oil also had a bearing on the stability of soap made from it ; thus soap from raw groundnut oil and tallow was usually far more stable than that from soap stock (G.V.R., S.A.S.), and rancidity products from an oil are no doubt carried over into soap (N.B.N.).

The *peak rancidity* of fats came in for speculation ; the speaker's own figures for linseed showed that peroxides did not accumulate indefinitely and were indeed found to be unstable even at room temperatures (J.S.A.). It would be interesting to see if there were any maximal " nitrogen " rancidity (G.S.S.). Investigation of a five-thousand year

old Egyptian tomb fat had shown it to be completely odourless ; peroxides in themselves are not believed to be odorous,-but only their further breakdown products like aldehydes, ketones, acids, etc., though even these would no doubt volatilize completely with time (K T.A.). The whole question of *smell* was of great interest recent work had shown that any smell was a composite of a finite number of discrete odours, and that a nose fatigued to some component could be used to determine the presence of that component in another smell (K.T.A.).

ROSIN IN VARNISH AND SOAP INDUSTRY

by

MR H. H MATHUR

(*National Chemical Laboratory, Poona*).

Rosin is obtained from several species of the pine tree distributed all over the world. On distilling the oleo-resins tapped from the living pine tree, the volatile matter that distils over is collected as gum turpentine and the residue is gum rosin By the distillation or solvent extraction of pine stumps, wood rosin is obtained, and can be refined by a pair of immiscible solvents such as furfural and a petroleum hydrocarbon, to remove the coloured and oxidized material.

The distillation of oleo-resin is being carried out in the Indian Union near Bareilly, and another factory is being set up at Nahan in Simla Hills. There is ample scope for development.

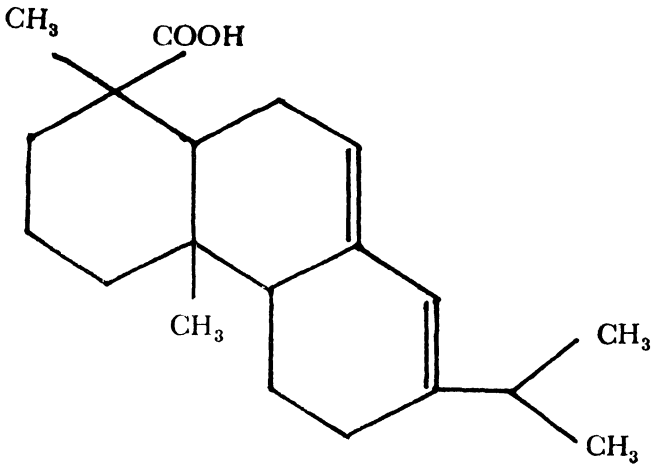
Amongst the important applications of rosin are paints and varnishes, soaps and disinfectants, paper-sizing materials, adhesives and plastics.

Composition

Rosin is composed of approximately 90 per cent acidic and 10 per cent neutral materials. The acidic components consist of complex terpene acids (chiefly abietic and pimaric) or of their corresponding anhydrides, while the neutral matter, besides unsaponifiables, consists of esters or possibly lactones. The resin acids are structurally similar in that they all contain a more or less saturated phenanthrene nucleus with a methyl group and a carboxyl group on the 1-carbon, and an angular methyl group on the 12-carbon ; the nature of the substituents on the 7-carbon as well as the degree and position of unsaturation varies from case to case.

The largest portion of the resin acid fraction, about 50 per cent. consists of abietic acid, levopimaric acid and neo-abietic acid, in all of which the substituent on the 7-carbon is an iso-propyl group contain-

ing two ethylenic linkages—the individual members differing only in the position of the conjugated system ; the chief isomer, abietic acid, is indicated in Fig. 1.



ABIETIC ACID

FIG I

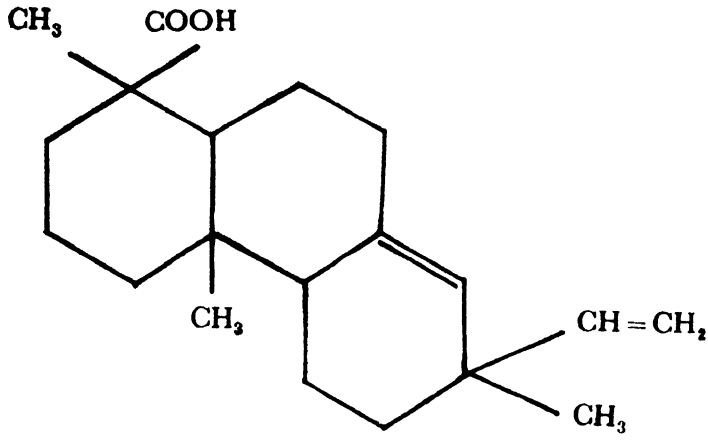
Approximately another 20 per cent is made up of two stereoisomers, namely, dextropimaric and iso-dextropimaric acids, which carry a methyl and a vinyl group in the 7-position (*see* Fig. II, *page* 153).

The remainder of the resin acid fraction consists of tetrahydroabietic acid, dihydroabietic acid and dehydroabietic acid.

The major part about three-quarters of these resin acids seem to exist in commercial rosin in the dimolecular form only This statement is supported by the observation that the molecular weight of abietic acid (about 300) rises on heating and reaches a maximum figure of 600, beyond which it does not go on further heating, while the molecular weight of commercial rosin also lies between 520 to 540

Chemical Properties

The chemical properties of rosin revolve chiefly around the carboxyl group and the unsaturation of the resin acids. While the carboxyl



d- PIMARIC·ACID

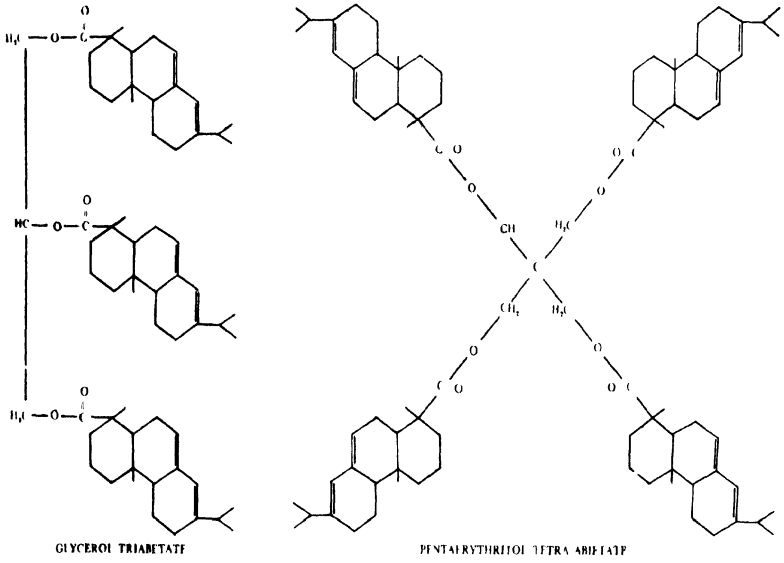
FIG. II

group is capable of salt-formation and esterification, its reactivity is greatly influenced by the fact that it is attached to a tertiary carbon, which again is a member of the bulky ring system On the other hand the existence of most of the unsaturation in the form of a conjugated diene system allows of a wide variety of reactions such as the addition of maleic anhydride, hydrogen, oxygen or phenolformaldehyde condensates, as well as rendering the resin acids susceptible to polymerisation and isomerization.

I shall now pass on to the commercial uses of rosin in varnish. As a varnish resin, colophony has many defects. An oil varnish containing rosin has a brilliant gloss when freshly applied but this rapidly disappears especially on exposure to weather. The dried film is brittle and is rapidly destroyed by abrasion. Such a film exposed to air gradually crumbles because of oxidation, with the formation of a certain proportion of water–soluble compounds which lead to permanent whitening of the film by the action of water. In addition, the lack of resistance to moisture causes excessive " blooming " even when the varnish is not actually exposed to the weather. The high acidity of rosin prevents its use with basic pigments.

On the other hand, rosin is a powerful dispersing agent and its presence in certain types of varnish is therefore advantageous to the extent that it increasees the stability of the product It also acts as a flux and facilitates the "running" of the harder resins. Also, the economic advantages of using rosin in varnish manufacture materially encourages experimentation and research with the object of reducing, if not entirely eliminating, these defects which restrict its use in varnishes

Ester gum and lime-hardened rosin have long been in vogue, but these products, although an improvement on rosin have poor resistibility to water and dilute alkaline solutions. The pentaerythritol ester



GLYCEROL TRIABETATE

PENTAERYTHRITOL TETRA ABIETATE

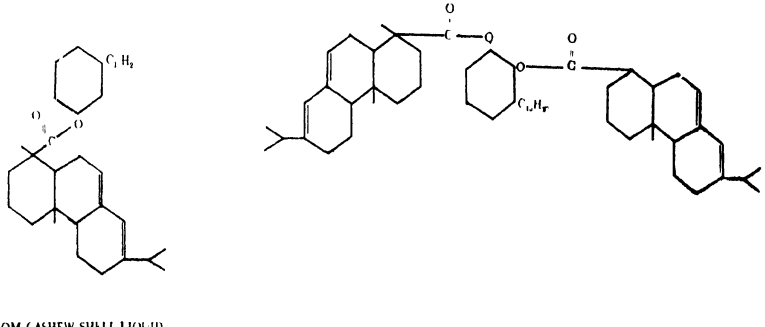
FIG III

(*see* Fig. III). of rosin is a modern improvement on ester gum inasmuch as it has a melting point some 25°C higher and has a greater resistance to heat and saponification This can be well understood by the graphic formula The glycerol ester has a relatively open structure, laying open the ester groups to hydrolytic attack In contrast, the ester groups of pentaerythritol tetraabietate are protected on all sides by the bulky rosin nucleus. For improved retention of properties on aging, hydrogenated rosin esters have also been employed.

As a result of the work done in the National Chemical Laboratory, Poona, modified rosins have been prepared whose varnishes have good resistance to water, dilute acid and alkali solutions, and common solvents Also, these varnishes are rot-proof. Such modifications have been effected through esterification (the most important resin-forming reaction of rosin) with phenolic substances like carbolic acid, cresols, cashew- and bhilawan-shell liquids, and hydroxy-acids like shellac acids. Semi-solid to solid resins have been prepared which are compatible with oils and are soluble in petroleum hydrocarbons, vegetable turpentine and other suitable solvents. Air-drying oil varnishes and lacquers have been prepared from these resins and tested for their water, acid, alkali and solvent resistance.

The carbolic acid and cresol modified rosins are hard, pale brown resins which give light, pale-coloured oil varnishes having fair resistance to cold water and dilute acid (2N sulphuric) but have poor alkali resistance, though better than that of ester gum varnish These varnishes are very well suited for cedar wood furniture, sports goods and high class toys

The cashew- and bhilawan-shell liquid modified rosins are soft, dark-coloured resins, the oil varnish from which though darker in colour has very good water resistance (Fig IV)



FROM CASHEW-SHELL LIQUID

FROM BHILAWAN-SHELL LIQUID

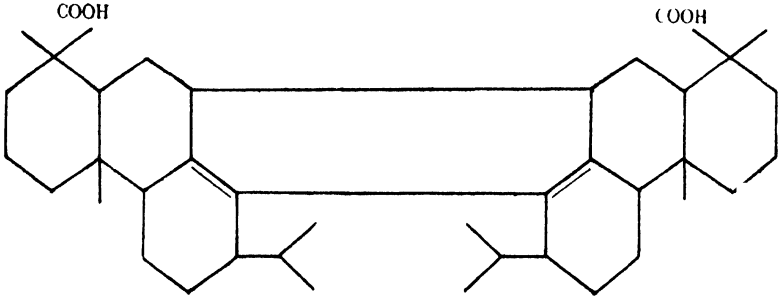
FIG IV MODIFIED RESINS

A wooden plate with a single coating of this varnish could stand in cold water for 18 hours without any appreciable loss in gloss. The

resistance to dilute acids, alkalies and organic solvents is also quite good. This varnish is ideally suited for outdoor purposes where it is liable to be exposed to natural weathering agencies.

Another method of approach for increasing the molecular complexity and hence the melting point of rosin esters is by attacking the conjugated unsaturation of resin esters.

Resin acids can be polymerised to yield dimers which are dibasic acids, the esters of which have higher melting points and greater resistance to oxidation than the corresponding monomer esters. (Fig. V)



ABIETIC ACID DIMER

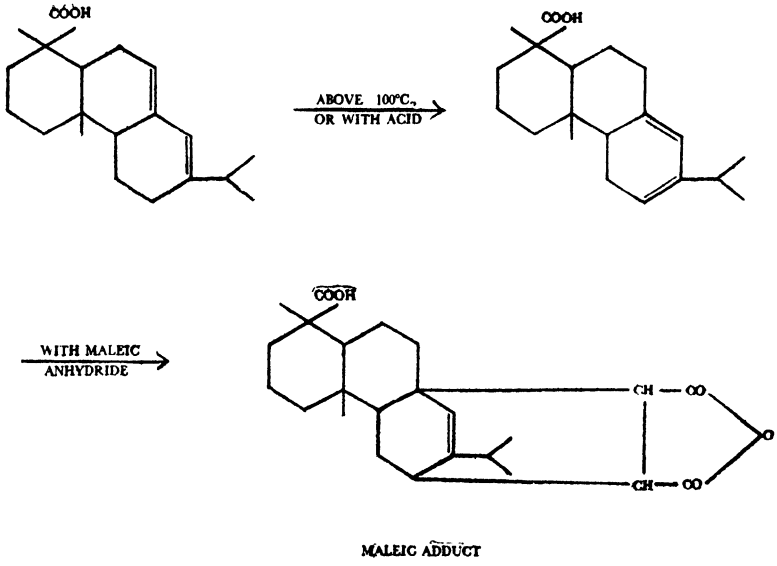
FIG. V

Abietic acid is isomerized to levo-pimaric acid on heating and the isomer forms an adduct with maleic anhydride at room temperature (*see* Fig VI, *page* 157). Since this adduct is a tribasic acid, esterification with alcohols of a functionality of two or more leads to a three-dimensional polymeric molecule.

Another method of converting rosin to a polybasic acid is by condensation with phenol-formaldehyde condensates.

The other important application of rosin is in the soap industry.

Sodium rosinate is an important constituent of the majority of household soaps due to its low price and the free availability of rosin. Rosin soaps are freely soluble in water and foam readily ; further, the addition of 2-3 per cent. of rosin to toilet soaps helps to avoid rancidity.



MALEIC ADDUCT

FIG V.

The disadvantages in admixing rosin are that the resultant soaps have a lower titer, have a tendency to darken, yield higher unsaponifiables, have poor wetting and detergent properties, roughen the skin and leave a gummy feeling. Admixture of hydrogenated rosin in soaps overcomes to a great extent the disadvantages of the original rosin and also gives a harder soap with a good body that does not crack. This was noted independently by Paul Mayfield (Soap, sanit. chem., 1943, **19,** 69-70) and Boiglin (Oil & Soap, 1943, **20,** 77-84) and has been further supported by Gupta, Phadnis and Aggarwal of the National Chemical Laboratory, Poona, in their investigation on the substitution of coconut oil in soaps.

Rosin soaps are definitely reported to possess greater germicidal properties than fatty acid soaps and hence are advantageously employed in disinfectants

Further investigations on the use of rosin in varnishes and soaps on the lines indicated above are in progress in the National Chemical Laboratory of India, Poona.

(*Wednesday* 16*th August* 1950).

DISCUSSION

The following participated :—

Dr. J. S. Aggarwal, National Chemical Laboratory, Poona.

Mr. G. V Ramaswami, Vegetable Oil Factory, Mettur

Dr. S. A. Saletore (President), Central Laboratories, Hyderabad-Deccan

Dr. N Shanmukha Rao, Central Laboratories, Hyderabad-Deccan.

Dr. G. S. Sidhu, Central Laboratories, Hyderabad-Deccan

Dr P. M Bhargava, Central Laboratories, Hyderabad-Deccan.

Mr Bharat Bhushan, Central Laboratories, Hyderabad-Deccan.

Mr. I K. Kacker, Central Laboratories, Hyderabad-Deccan

The *properties of the* several *modified varnishes*, with respect to water-resistance, gloss and hardness of the dried films, were enquired of (S A S), the speaker (H H.M.) replied that they were apparently good, but owing to lack of equipment the tests had been only empirical

The *anti-corrosive properties* of the *condensation products* of rosin and cashew-shell oil were the subject of a question (G.V R.), the speaker (H.H.M.) replied that the anti-corrosive properties associated with cashew-shell oil were carried over into the condensed product In reply to another query (I K.K), he stated that though equimolecular proportions of rosin (containing one carboxyl group) and cashew-shell liquid (containing one hydroxyl group) should be enough for condensation, the large degree of polymerisation accompanying the reaction meant that more of the latter was required than theoretically necessary

Many suggestions were forthcoming to explain the *relative inertness of the carboxyl group* of the acidic fraction of rosin Steric hindrance appeared probable (G.S.S.), and the high molecular weight and low mobility of the molecule were doubtless contributory (N S R); it was possible also that the resin first formed by spontaneous polymerisation covers the whole molecule and renders the carboxyl groups incapable of reaction (B.B.). [Esters of rosin acids are formed with difficulty mainly because the carboxyl group is attached to a tertiary carbon atom, as stated in the lecture —Ed]. Since associated vinyl compounds are highly prone to polymerisation and would mask the reactions occurring with acidic compounds, the use of pure isolated

abietic acid derived from rosin for theoretical studies on pentaerythritol condensation, etc., was suggested (G.S.S.). It was however pointed out that even pure abietic acid resinifies in 4-5 hours at room temperatures owing to the presence of conjugated systems ; in any case the commercial product contains some 90 per cent. of the acidic fraction, and could conveniently be used even for theoretical studies (I.K K.).

Since polymerisation was the most characteristic feature of rosin, a number of interesting points arose It was argued that *neo-abietic acid* has a vinyl chain and was *highly prone to polymerisation* in consequence, and that this might hinder the various reactions described by the speaker had any attempt been made to stop such polymerisation (B.B) ? The speaker (H.H M) replied that in the context both polymerisation and addition products were desirable , no attempt had been made to distinguish between the two types of reaction and the overall progress of the latter had been followed by means of acid value determinations Doubts were raised regarding *the feasibility* of many *of the addition reactions* described, since polymerisation of rosin was so rapid (B.B.) , the speaker (H.H.M.) said that polymerisation at room temperatures was not so rapid as had been suggested and that addition reactions did occur. The nature of the dimer acid produced on polymerisation was only inadequately known (I K K) , it was suggested that these polybasic dimers would no doubt yield interesting products on condensation with glycerol, etc. (P.M.B.)

Suggestions of various kinds were made. The *four assymetric carbon atoms* occurring in abietic acid were pointed out as worthy of study (N.S.R.), and *the use of rosin acids for the preparation of biologically-active compounds* was mentioned (B.B.). The *use of the term 'vegetable turpentine'* was likely to be misleading since this comprises two distinct products, ' wood turpentine ' and ' gum turpentine ' , was anything known regarding the *composition of* dry-distilled rosin, the so-called *rosin oil*, which was much used in the varnish industry (B B) ? In reply it was stated that these rosin oils contained decarboxylated, and possibly dehydrogenated, products derived from rosin (J S A) Finally, it was stated that over 80 per cent of the constituents of rosin were crystalline acids which had no role in the drying of rosin, and the product as a whole was in fact hardly used today, though the speaker (H.H.M.) maintained that these crystalline acids were unsaturated, prone to oxidation and polymerization, and played a part in the drying of rosin

in varnishes. Of the derivatives, the *maleic anhydride adducts* appeared to be the *most promising*, yielding a better rosin with good drying power and high potential glass, and should be concentrated upon (B.B.) The speaker (H.H.M.) agreed, but said that the aim of the paper was to indicate generally the lines of work being followed for the modification of rosin for use in varnishes.

FATS IN DAIRY INDUSTRY

by

Dr. K T. Achaya

(*Central Laboratories, Hyderabad-Dn.*)

We are all aware that the milk of animals contains fat in varying proportions ; in Indian diary industry it is with the fat of the milk of cows and buffaloes with which we are primarily interested The research and production problems connected with fats arising in the dairy industry are in a sense peculiar to the industry, and the average fat chemist is not often concerned with them I thought I should endeavour today to indicate a few such, mainly research, problems as being of interest or profit to our conditions I shall proceed with fat in the state of milk, of curd, and then mainly as itself, *i.e.*, as butter or ghee, dealing with a somewhat heterogeneous set of phenomena on the way.

Fat is held in milk as dispersed globules in a microscopic state, and contributes in some measure to the white or creamy colour of milk It has long been known that the fat is held in emulsion by means of a layer of some sort enveloping it, but till recently little was known about this layer, though it was more or less tacitly assumed to be of protein nature. Work in progress both in Holland, an enterprising dairy country (V Nederveen and Ernsting) and in the U S A. (Jenness and Palmer) indicates the nature of this membrane surrounding the fat globule in milk. One report indicates that the membrane contains phospholipids and a protein-sugar complex, probably a mucin, while in another instance serological tests have been used to indicate that the membrane contains both casein and globulin. Even more interesting is the report that on crystallisation of the membranous material from alcohol, samples of a phosphorus-free triglyceride with very constant properties were repeatedly obtained It melted at 52-53°C., had a saponification equivalent of about 280, and an iodine value of 5-7 , it was concentrated in washed cream serum and had special affinity for the membrane phospholipids. Clearly much of interest is likely to transpire in the future regarding our knowledge of this membrane. Moreover, it has been shown (Rangappa and Banerjee, India) that

the isoelectric point of fat globules in milk is less on the acidic side (pH 4 5-4. 6) than that in cream pH 4. 3), and it has been suggested that this is sufficient to prevent the fat globules from coalescing ; on addition of a starter and subsequently increasing acidity, this charge is increasingly neutralised and the globules coalesce and rise

Another interesting theory regarding the fat of milk has recently been brought forward by Kon and co-workers at Reading They find that whereas vitamin A in milk appears to be in true solution in the fat, the carotene in milk fat appears to be in some way dependent upon the globule size, or rather the globule surface The smaller the fat globule, the larger the number of such globules going into a unit weight of fat, and the larger therefore the carotene content per unit weight of fat Will some such mechanism, always bearing in mind physiological specificity, account for the high vitamin A contents of buffalo ghee per gram compared to cow ghee, and the total absence of carotene ? It was shown many years ago (Kothavalla and Sunawala, India) that the fat globules of buffalo milk are very much larger (5. 4 5. 7μ diameter) than those of cow milk (2 9-3 4μ diameter) though somewhat smaller in number per unit volume of milk (70 per cent) A simple calculation will show that nearly five times the number of fat globules of cow milk are required for any fixed weight of fat than of buffalo milk, and perhaps the carotene contents of the two milk fats may be partly dependent upon this fact

At this point I shall digress briefly from the main trend of this paper. The carotene and vitamin A contents, in μg./g. and in I.U./g., of specimens of Indian cow and buffalo ghee examined by us were 18 and 8 respectively (cow ghee), and nil and 16 (buffalo ghee), while average figures for English cow butterfat are 7 and 24. These figures represent fine Indian specimens from a diary herd and are indicative of the good vitamin quality of our better butterfat Moreover, the lactational yield of the Indian cow and buffalo in good diaries is of the order of 3000 lb , and 4000lb., which compare very favourably with the 4500 lb. average for Europe ; it was also of great interest to note that while the fat contents of the milks of western breeds of cow were about 3.7 per cent. on an average, that of the Indian cow and buffalo were 5 1 and 8.5 per cent respectivley. Our much-maligned Indian cattle prove on closer acquaintance to be well worth cultivating in more than one sense !

Let us pass on to the next stage in the evolution of milk fat. In India, a starter is added to milk with the production from lactose of lactic acid, and the coagulation of protein at its iso-electric point (pH 4. 6), side by side with the coalescing of fat as already explained The curd thus obtained contains of course all the fat, but the distribution of this fat in dahi (curd) is not uniform, in fact very much the contrary Anantakrishnan and Kothavalla (India) have found that irrespective of surface area the fat distribution in a column of dahi is dependent on the height only, the largest proportions of fat being at the top and the smallest at the bottom Typical figures for four such 'layers' were 49, 24, 20 and 8 per cent As the height of the column was reduced, much more of the fat rose to the top layer —90 per cent when the height was only 3 cm Why should this be so ? It is possible that the fat in milk during fermentation would normally all rise to the top and occupy as little volume as possible, but that the viscosity of the rapidly-coagulating fluid prevents such action and that therefore a graded column is produced Tests with watered milk of low viscosity should help prove the point, which is certainly of more than merely theoretical interest.

We shall now pass on rapidly to the state of ghee. Dahi is diluted, churned into butter, and the butter heated with loss of water to form ghee Ghee constitutes eighty per cent of all milk products in India and is of outstanding interest scientifically and economically I shall indicate a few recent trends of work likely to be of interest to us in India.

The changes occurring on heating butter into ghee have been studied with especial thoroughness by Swiss workers (Ritter and Nussbaumer) who state that during the intense foaming which occurs for the second time in the cooking process, and which is usually indicated as the 'finish of reaction' by text books, lecithin which is present in the brown residuum passes into true solution in the hot fat in the form of foam, and is of course often observed on cooling hot ghee. Some of it however remains in solution and gives the fat the well-known brownish colour on heating fat which is free from lecithin remains white on heating Moreover it has been found, mainly in America (Dahle and Josephson), that butter heated at temperatures from 100-200°C showed tenfold increases in keeping quality over fat separated from butter held at 120°C In separate experiments, neither phospholipid nor membrane protein gave protection, but various combinations of phospholipids with sugars and proteins were partly effective, while dried skim milk was excellent. The mechanism of stabilisation, which

is operative in most Indian methods of ghee-rendering and is not implied in methods involving low-temperature removal of fat and of moisture subsequently, is not understood, but appears to be a protein-phospholipid reaction . it is clearly of great interest to us in India. Further, while the aroma of butter has been traced by careful work to diacetyl, that of ghee is still unknown, though Banerjee and co-workers (India) attempted it and traced it to ghee ' scum ' but no further. The whole question of smell is of great interest

On keeping ghee, it usually crystallises in more or less granular form and this has been the subject of some excellent research from Germany (Mohr and Baur) and Switzerland (Ritter) Coarse crystallisation is produced by higher temperatures of cooling without seeding, and fine crystallisation by low temperatures, the latter effect being increased by rapid cooling In coarse cooling the fat tends to form agglomerates, which on careful heating and suitable cooling at low temperatures, forms fine crystals which radiate from central points to produce a complex matrix , differences in fat quality are not due to the nature of crystals but to their arrangement The layer which forms on top of ghee is due to shrinkage on sudden cooling, when air is trapped in the fat, and is thus ultimately due to insufficiently fine crystallisation , it is usually remedied by initial stirring.

In Australia and New Zealand particularly (Loftus-Hills, Wiley and Coombs , McDowall), and to some extent in the U S A , the commercial production of dry butterfat or ghee, packed in tins, is a growing industry designed in general to suit the western palate Thus the ' tropical butterfat spread ' developed in Australia during the war consists, as percentages, of ghee 90 salt as preservative 2, skim milk powder as antioxidant 4, hydrogenated fat (to raise the melting point) 3 to 4, and diacetyl as flavouring 0 2 parts per million The product is stated to have a smooth texture and to be as spreadable as butter, while 20 per cent of water could easily be incorporated into the material, clearly butter-like qualities were desired, but the method shows that the commercial production of ghee in tins is an entirely feasible process. New Zealand produces a ghee by centrifuging butter and using a rotary cooler, while in Germany high-temperature removal of water is claimed to give commercially feasible results. In most cases a small amount of very hard (hydrogenated) fat is blended to give higher melting points, of the order of 40°C., to the product.

I have mentioned the addition of salt in the Australian process for purposes of preservation and taste. It was found that commercial salt had marked pro-oxidant effects which were removed by roasting the salt or by mixing it with a small proportion of sodium sulphate. This was eventually traced to the presence of about 0 1 per cent. of magnesium chloride which acts as a heterogeneous catalyst only in the solid state and not in solution. This experience has obviously much interest for us in India where commercial salt is often used for antioxidant effects in ghee.

I should like to make a passing reference to the much-debated question of the vaccenic acid content of ghee. This acid, which is Δ11-12 octadecenoic acid and isomeric with oleic, has been reported to be responsible for better growth after much laborious work, especially by workers from Holland (Boer and coworkers), while equally strong denial of the growth-promoting activity of this acid comes from various American workers (Elvehjem, etc.), one report even states that the vaccenic acid fraction possessed marked biotin activity for certain species of *Lactobacillus* (Daubert) The true explanation for this controversial question has yet to be settled, but I thought I should mention it in passing.

At this point I shall digress again to briefly make some points regarding fat absorption. As first shown in the classical experiments of Lawes and Gilbert, fats are mainly produced in the animal body from carbohydrate material, and ingested fat comes only slightly into play in fat-formation ; under unusual circumstances, protein can also function in the body as a fat-former. Also, there is no positive evidence so far of the superior value of one fat over another, provided the melting point of the fat is below about 47°C. ; since all fatty acids are oxidised in the body it is difficult to imagine how one fatty acid could be superior to another, and all would appear to be more or less equally useful to the body—excluding of course specific ones like the essential fatty acids.

The pressing problem is of course more milk and more milk fat. Recent work has shown that the fat content of milk is related only very slightly to the fat content of the diet, but very markedly to the protein content of the diet Evidence has also been brought forward to show that the shortest way to increase butterfat production is by breeding to increase milk yield ; simultaneous increase in both milk yield and

fat content, two genetically independent factors, is difficult, and the former is recommended in preference to the latter (Krizenecky, Czechoslovakia)

We have come full cycle, following the fat of milk through its various phases and touching various research problems on the way Numerous others exist of course, but most of those outlined today, it may be claimed, are of somewhat special interest to conditions in our country.

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(*Thursday*, 17*th August* 1950)

DISCUSSION

The following took part in the discussion —

Dr J S Aggarwal, National Chemical Laboratory, Poona

Dr M. R. Mandlekar, Department of Industries, Bombay

Mr G V. Ramaswami, Vegetable Oil Factory, Mettur

Dr S Husain Zaheer, Central Laboratories, Hyderabad-Deccan.

Dr S A. Saletore (President), Central Laboratories, Hyderabad-Deccan.

Dr N Shanmukha Rao, Central Laboratories, Hyderabad-Deccan.

Dr G. S Sidhu, Central Laboratories, Hyderabad-Deccan.

Mr N. Bhojraj Naidu, Central Laboratories, Hyderabad-Deccan.

Mr I. K. Kacker, Central Laboratories, Hyderabad-Deccan.

Mr A Rahman, Central Laboratories, Hyderabad-Deccan

Mr L M. Srivastava, Central Laboratories, Hyderabad-Deccan.

The yields and fat contents of Indian cows and buffaloes quoted by the lecturer were the subject of some comment The President (S A.S) disagreed with the lactational yields quoted and believed that in general cows of English strains gave 17-18 times as much milk as an Indian animal. In answer to a question (A.R.), the speaker (K.T A.) stated that under badly-tended, village, conditions a survey had resulted in lactational yields of 900 lb per cow and 2000 lb. per buffalo ; but he had taken figures from Indian dairy herds for comparison with averages in Britain since in western countries the average is fairly close to

the best, unlike in India. It was pointed out that this did not give a true picture of Indian conditions (S.H.Z.) The speaker (K.T.A.) replied that his primary aim was not to picture these conditions, but to judge English and Indian milk-fats on a comparable basis so as to bring out physiological facts of interest in respect especially of carotene and vitamin A contents. Questions were asked regarding the high fat contents of Indian cow and buffalo milk (L.M.S.), had heredity any part to play (A.R.)? The speaker (K.T.A.) replied that several factors were involved: climatic factors, since all tropical countries showed this phenomenon of high-fat milk, while even in western countries during abnormally hot summers the same feature was noticed, the body size of the cow might well play a part, even the frequency of watering had been found to affect yields and fat output! The President (S.A.S.) remarked that the playing of music to cows, so he had read, affected milk yields, the three main factors involved in milk yields were probably food, climate and feed.

Goat milk was enquired about, the speaker (K.T.A.) gave a short account of the different Indian breeds and stated that they yielded about 400 lb. of milk per lactation with a content of fat of 4-5 per cent. The milk had a flavour attributed variously to free grazing, uncleanliness of animals and the indiscriminate herding together of the sexes, the President (S.A.S.) added that lack of udder cleanliness was mainly responsible.

The physiology of fats came in for discussion. In answer to a query (S.H.Z.), the speaker (K.T.A.) briefly summarized the work of Schonheimer and Rittenberg using deuterium to follow fat metabolism. Hydrogenation and dehydrogenation could both occur, also homologous breakdown and building-up, fats in the body are in a constant state of flux or dynamic equilibrium, in which the 'half-life period' of a particular acid was of the order of five days. Also, it had long been known that fats could not be reduced by fasting below a certain level, usually about 33 per cent. of the bodyweight, since protoplasm contains fat as an essential constituent—the 'element constant' of Terroine. The interrelationship in the body of the fats, the carbohydrates and the proteins was described (N.S.R.), alanine yielded pyruvic acid, which was a breakdown product of fats following β-oxidation; pyruvic acid was the precursor of lactic acid, which was produced during muscular oxidation by utilization of glucose, itself produced

from glycogen stored in the liver. When fats are exhausted in the body, proteins are mobilized , on the other hand, *e.g.*, game are known during the sugarcane season to fatten on carbohydrate material Speaking on the nutritive value of the fats, it was pointed out that only very small quantities of the essential fatty acids, linoleic, linolenic and arachidonic, were needed by the body and that their deficiency in a normal diet would be a rarity , the rate of absorption, in the early stages, of the lower fatty glycerides found in butterfat was faster, but at later stages all glycerides were absorbed at equal rates (G.S S) The President (S.A S) also thought that in the present state of our knowledge it could only be stated that we were ignorant of the roles of the individual fatty acids, and it would be incorrect to say that one fatty acid was as good as another [Indeed, very recent work indicates that acids of different chain lengths are differently metabolised, the longer chain acids giving carbon dioxide by Krebs' cycle mechanisms, and the shorter acids yielding primarily acetoacetate —Ed]

The destruction of vitamin I in the clarification of butter into ghee varied enormously, the speaker (K T A) stated in answer to a query (G V R) , he quoted a typical figure of 22 per cent. destruction on 10 minutes cooking at 120°C. One speaker (N B N) was of opinion that earthen pots were superior to certain metals for conservation of the vitamin in ghee during storage The value of certain *indigenous materials for preservation* excited great interest (N B N) ; one speaker (J.S.A.) had found that many spices had antioxidant properties, including the betel leaf ; the President (S A S) was of opinion that most of the substances added in India during clarification were for purposes of flavour, though in vegetable oils he had found that betel leaf was without antioxidant effect but that pepper exhibited it to some extent ; the lecturer (K T A) referred to the work of Rangappa and Banerjee on ghee clarification and said that no doubt some substances were with effect and others without Salt was used in India mainly for clarification and not as an antioxidant, it was stated (I.K.K.) ; no doubt a small part would dissolve in the water in fat and may be a pro-oxidant as described in the lecture (K.T A)

The aroma of ghee, a question raised in the paper, was stated by the President (S.A S) to be due to a mixture comprising nine or ten constituents, including aldehydes, ketones, ethers, butyric acid and diacetyl. He had found that ghee from different areas in India differed markedly ;

the product from Bihar consisted of hard crystalline grains with a liquid portion above and had a greenish tinge, while that from Madras had hardly any crystal structure and was slimy in appearance The *peculiar flavour of powdered milk* was enquired about (M.R.M.) ; the speaker (K.T.A.) stated that it could be caused by the use of copper equipment during manufacture or may be due to a fat-protein interaction , much work on the subject had been done by Lea

Finally, attention was drawn to the *usefulness of casein* for plastic manufacture ; also, after casein had been precipitated from whey, milk-sugar could usefully be obtained by evaporation (N.B.N.)

SYMPOSIUM ON RESEARCH & INDUSTRY

Edited by

Mr. A. RAHMAN

President: Dr. B. S. KULKARNI, Reader, Applied Chemistry Department, Osmania University, Hyderabad-Dn.

President's introductory remarks.

Commenting on the purpose of the joint symposium on " Research and Industry," the President said that it was arranged to discuss broadly some aspects common to many industries. Topics under this section were of a general nature and would give considerable scope for generalisations and bring many controversial issues to the surface It was hoped that a general cross–section of the views expressed would be widely representative and that all views would be accommodated.

He further said that in today's Session (14th August) both the papers, *viz.*, " Place of Industrial Research in the Development of Chemical Project," and " Choice of Raw Materials," would first be presented and followed by a joint discussion.

PLACE OF INDUSTRIAL RESEARCH IN THE DEVELOPMENT OF CHEMICAL PROJECT.

by

DR. B. S. KULKARNI

(*Applied Chemistry Department, Osmania University Hyderabad-Deccan*).

The paper is selected to give a general idea about the nature of pilot plant research and its relationship with industry and institutional research. It was chosen because it was felt that " Research in Industry," a topic of great interest, is mostly confined to project development.

Project development is a factory term, also adopted by the Chemical Engineering Science, which is applied to the overall operation in implementing an idea for a chemical product or process to the actual large scale production. The operation is also spoken of among the factory executives as " going full scale " or " scaling up from conception to commercialisation." It embraces all types of research including laboratory research, development research, market research, etc.—in fact almost the whole research activity of an industrial concern So much technical and economic literature has of late gathered around this subject that even an adequate summary of one single aspect may become difficult. Choice of a research programme, responsibilities of a management in financing and budgeting a development project, methods of going full scale with the fewest head-aches, and of elevating results from the laboratory bench to the pilot plant, are some of the topics which are receiving exhaustive treatment at the hands of experienced chemical engineers and factory managers. All productive research, whether carried out in an institution or a factory, has directly or indirectly one aim, namely, commercial exploitation. What brings about a noticeable difference between the two is the difference in outlook and the difference on the relative emphasis on mainly three factors—efficiency, economy and speed In institutional research such as that carried out by government departments, universities, research associations, foundations, etc., actual factory conditions are more or less absent ; so also are the survival objective and the profit motive. The result has been that institutional research even in the most advanced countries

has always remained a follower rather than a leader in the field of industrial research. We in India are at present in the very elementary stage of institutional research, since factory research in India is almost non-existent. As many of us are engaged in research of the productive type which ultimately has to pass through the stage of project development, there is much for us to learn from the pages of industry. The present paper can at best describe very briefly and objectively industry's view-point and procedures in development research, in the hope that interest would be awakened and our institutional research would be oriented more and more on the factory lines.

The industrial approach, as differentiated from the institutional outlook, will be best appreciated in the context of the tremendous emphasis which industry lays on research and the colossal investments it makes in project developments. Many branches of chemical industry were created by research, such as the dyestuffs, the plastics, rayons, nitrogen fixation, petroleum, etc., No other industry has been more dependent upon investigations and technical developments in a rapidly changing scene. As many authors have expressed, the only thing that does not change in chemical industry is the change itself. Any firm in chemical business which stands still, that is, undertakes no research, actually moves backward relative to its competitors. America speaks of research itself as a billion dollar industry (1). Investment in research in 1947 amounted to about 1200 million dollars and the target set for 1957 is roughly two-billion dollars or about 2 per cent of the national annual income of America. More than 130,000 research chemists and engineers are working in nearly 2500 research establishments (2). Chemical industry accounts for about one-fourth of these totals. In the list of America's hundred largest industrial corporations there is not one which does not maintain a research staff and laboratory and support an effective research programme. As Soule (3) put it, " the biggest industrial gamble is to do no research at all "

Within the chemical industry research expenditure on an average amounts to 2-3 per cent of the sales, even though some firms are known to have spent more than 20 per cent. of their net income on research. Compared to the total plant cost, including the whole fabrication, research and development take away about 12-67 per cent depending on the nature of the product or the process (4).

Expenditures on institutional research on the other hand amount to only one-sixth of those made by private enterprises. In fact at one

time it was seriously discussed whether private industry is not endangering the freedom of industrial research (5) It is, therefore, industry which is setting the pattern of modern research (3)

All these research developments in industry have not been haphazard or wild, as otherwise there would not have been a never-ending stream of new products and processes pouring out in the market every year in the smoothest possible manner and at the fastest speed The largest contributing factor to the consolidation of the principles of project developments and their translation into the modern technique has been the emergence in the present century of chemical engineering as a fullfledged science Project development in fact is the crux of the Chemical Engineering principles and philosophy Previously a chemical process was viewed in an isolated manner partly by a research chemist who originated the idea and partly by an engineer who executed it, so that on account of lack of co-ordination and outlook between the two, the process had to blunder through many costly trials and errors before results could be obtained on a factory scale These two outlooks have now been co-ordinated by a chemical engineer who does not look at a particular process in its individuality but breaks all processes into a series of unit processes and unit operations, such as filtration, evaporation, hydrogenation, nitration, etc In project development, the chemical engineer has to deal with principles and technique not of a single unit operation or unit process connected with a single chemical process but with as co-ordinated an assembly of these as can possibly occur in all processes Therefore in the translation of a laboratory idea into a planned process the chemical engineer becomes the central dominating figure, and what prevails throughout the project is what Kirkpatrick described as the "chemical engineering outlook" of this Chemical Engineering Era (6)

In actual plant practice, the tasks and problems connected with research schemes are called "projects" Usually in order to start any work on the problem, it is necessary to have a project set up covering this work A "project" is a written statement of what is desired to be achieved and how much it is expected to cost in time and money.

The preliminary work connected with the formulation of a project is primarily the function of the research and development departments in the company's organisational set-up. Very often these two departments are merged under unified supervision into one department of

development, whether the companies organisational set-up is of the "functional" type or of the "divisional" type (7). The internal structures of the development departments which have often been described in literature appear to be more or less uniform in most of the concerns. A more comprehensive and rational set-up has been recently suggested by Voorhies of the California Research Corporation, California Oil Gas Company (8).

The matter of choice for an idea which is to form the basis of a project is considered particularly important since there may be more ideas for research that can possibly be investigated or handled at one time. The idea must first be within the scope of the company's various objectives for research, which are often clearly defined, and within the sphere of its productive activity. Projects potentially capable of yielding results fall under the following four heads –

(a) New products and new processes

(b) Use of new products evolved by others in improving upon or economising in the production of the same article.

(c) Refinement in machinery.

(d) Refinement in processes

If there are many projects, management divides them into various groups in order to maintain proper development balance within the concern (1). These groups are classified as confining themselves to the following areas of research attack : (a) overall process areas *i.e.*, investigations into the inter-relationships of the various manufacturing processes carried out by the enterprise and integration of products and production, (b) intra-process areas which include research on specific components of a given process or product, (c) new methods and new product areas.

This type of grouping assists the top management in determining the emphasis that is warranted on a particular project, when to discontinue work or when to redouble effort Finally the idea must undergo a preliminary scrutiny of the development department where it is judged by mainly two criteria technical and economical. These may be paraphrased by the questions . will it work ? And will it pay ? Thus many ideas may get eliminated at this primary scrutiny or at any stage in the further development In short, in industry research conceptions become more ordered or tailor-made than free. On the final

score of the surviving ideas Bell (9) writes · " In the Cyanamide Company we are more than delighted if two of the hundred ideas eventually yield any substantial profit. If one in two hundred were to put us in a great basic industry with large profits over a long period we would now be the greatest company on earth."

If the conception, wherever its origin might be, is found suitable for further development, the project becomes an approved project with a small sanctioned appropriation to go up to the laboratory stage, and is ready to scale up the further development stages The basic principle of the scale-up is that the best managed research comprises succession of crucial experiments, a negative answer to any one of which automatically bars further exploitation of a barren territory. The earliest rational exposition of the steps in the project development was given by Whiting (10) who divided the process evolution into *five* distinct steps.

1. Beaker or Laboratory stage.
2. Small size model.
3. Large size model.
4. Semi-commercial plant.
5. Commercial plant.

With the progress of Chemical Engineering science and with accumulated experience, the scale-up has undergone many modifications. Various types of scale-ups have been discussed by Swezey (11); the one most commonly accepted consists of ·

1. Laboratory study.
2. Product evolution or feasibility.
3. Process study.
4. Pilot plant.
5. Semi-scale or full scale plant.

One may consider such a division as ordinary commonsense, but the success of the modern technique lies in codifying it into specific concepts and well-defined procedures.

The laboratory study or bench research begins with an intensive study of literature to isolate the idea. All thermal, chemical and physical data not available, such as type of reaction, quality and yield of product, solubility, temperature and pressure ranges, etc., are acquired

with the smallest outlay of money and materials. The research executive in charge of this type of work, who usually acquires in course of time a strong background of Chemical Engineering, will have already shared with the chemical engineers their rough visualisation of the possible unit operations and processes which will go to make up the final process on a large scale. The object of the laboratory study, therefore, is to ultimately prepare a workable qualitative flow sheet and collect as much of the design data as possible for the use of the chemical engineers. Thus the chemical engineer's envisaged design is always present in the background of bench research. In order that this type of work should maintain a correct outlook, it is the practice in many companies to make their bench research workers spend sometime in the factory, learning the manufacturing processes employed by them. Regular first-hand contact between factory and research is provided because it is as much a function of the laboratory to devise and improve manufacturing processes as to produce a new article in a test-tube. Secondly, far more rigorous economy is observed than is normally practised in institutional research ; for instance, if the required data could be acquired by the use of a 200 c c beaker, the research executive would hardly permit a 300 c c beaker to be used for the purpose. It is often incorrectly presumed that the chemical engineer has no connection with this type of bench work. Regarding the chemical engineer's part in this phase of work, Kirkbride (12) says :—

" Ordinarily chemical research in this case is done by highly trained chemists and physicists, although chemical engineers may do much of the experimental work. In any event, the chemical engineer usually appraises the process on the basis of the result obtained on the small laboratory equipment. Thus the Chemical Engineer follows the research work very closely even though he may not be directly involved in the experimental work It is very desirable that he be fully informed on the experimental technique, including methods of analysis. Also he should have a clear understanding of the limits of accuracy of the results obtained, and should make certain that all the data are being obtained which he needs to make his process appraisal "

After the laboratory study has been completed to the satisfaction of the chemical engineer, the next step in the scale-up is to determine the economic feasibility or commercial usefulness of the project. Important factors in this step have been variously described in literature (13, 14) This study is done by the chemical engineer in consultation

with the economic sections of the concern such as purchase, sales, cost estimation, etc., and includes judging the project on the basis of the sources of raw materials and their dispositions, possible by-products, approximate costs of manufacture, market conditions, patent situation, etc. For instance, if it is a new process to manufacture an existing product, then it must be critically compared with the present methods. Unless real advantages are apparent such as lower costs, safer operations, greater purity, more readily obtainable raw materials, etc., there is no reason to proceed further. The company's own specific interests in relation to the project will also be considered. Will the process or product tie in readily with the company's present operations ? Can the present sales organisation handle it ? Will there be special problems of packing and distribution ? In general this step is a continuation of the preliminary scrutiny with the addition of the laboratory data, and gives a definite indication whether there is sufficient chance of profitable commercial operation to warrant expenditure on further steps which are going to be far more costly There is no profit in spending money on an interesting but commercially useless proposition. Feasibility study is considered so crucial that often this stage has formed the graveyard of many ingenious research ideas.

It is only after the project passes the feasibility test that the process study is begun This is the central phase of the project development and is exclusively a field of the chemical engineer. The ultimate goal of this step is to prepare a design memorandum which will include

(a) quantitative materials and equipment flow sheets including piping diagrams,

(b) preliminary design of the commercial plant, and

(c) preliminary cost estimates

Often this study is designated as development research or engineering research but actually up to and including pilot plant study it is one continuity of industrial research. Process study views the laboratory result from a technological point of view by establishing clearly the unit operations and unit processes involved in the whole process, the type of equipment, their designs and sizes. For instance, we might find that a product which dries very satisfactorily in a laboratory desiccator may become quite a problem when handled in a rotary drier. Or what was achieved in the laboratory under high vacuum may become a headache with a commercial type of vacuum pump. Distilla-

tion which proceeded one way in a glass fractionating column may proceed entirely differently in a bubble cap column Similarly, semi-continuity or continuity cannot be ascertained in a laboratory study Then again there may be operations like petroleum cracking, high pressure and high temperature reactions, etc , which may require elaborate equipment not ordinarily thought of in the category of glassware. Corrosion problems which did not cause trouble so far may have to be given special attention. In general, in this stage three operations run parallel as data are accumulated

(a) Qualitative flow sheets gradually become quantitative

(b) Rough equipment designs gradually become firm plant designs.

(c) Order-of-magnitude cost figures pass through preliminary estimates into firm estimates.

It is also decided at this stage whether to incur the expense of a pilot plant or whether to straightaway elevate results to full scale by a little more intensive study

After the process study is completed the project enters the pilot plant phase if at all it is decided to set up one Pilot plant as a unit and pilot study as a phase are the most costly components of the research programme and require specially sanctioned appropriations. The subject of pilot plant has been considered so important that the journal, " Industrial and Engineering Chemistry," held an extensive symposium on the subject (15, 16). Pilot plant is a specific unit with a specific purpose. It is set up if there is a novelty either in the process or in any of its component equipments which cannot be judged by comparisons or similarities with the known existing processes. Before the pilot plant study is undertaken there should be no question regarding the workability of the process. The purpose of the pilot plant study is never to obtain data which *was not* obtained previously but which *could not* be obtained in the laboratory and the process studies. It is primarily to study the co-ordinated working of the assembly of all units which have previously been studied individually One may have carefully calculated the output per hour of a preheater and the input per hour of the next evaporator but their disposition may be such that the intervening pipes and friction factors may upset all the calculations. It is to know whether the rated capacity and the rates run uniformly throughout the process. It is also to obtain the type of data which is

generally affected by the time factor, such as the effect of accumulated impurities and corrosion rates, which cannot be ascertained without experimentation for prolonged periods. In short, the object is to collect sufficient overall data to determine if the process as now established will be both efficient and profitable on a commercial scale. Other objects of setting up the pilot plant are to study instrumentation, train the personnel and procure samples of the product to ascertain its reception in the market. Pilot plant study allows the design and the estimates of the final plant to become absolutely firm. The pilot plant therefore is symbolic of the total creative effort of the research workers and the chemical engineers. The chemical engineer objectively values pilot plant much more than the main plant because for him it is not the size of the plant or equipment but its shape and form and the process pulsating inside which is the reward of his labours.

Although the project itself passes hereafter on the straightforward and comparatively simple course of plant design and the equipment fabrication, the research programme has more or less reached its journey's end. Barneby of the Blawknox Corporation (14) summarises the philosophy of the project in the following four precepts :

(a) Break your project into a standard series of development steps.

(b) Proceed with a step only if proven economically feasible.

(c) Visualise the commercial plant before building the pilot plant.

(d) Make your mistakes as early in the programme as possible.

The above is only a brief outline of the industrial practice on project development and industries' outlook on research. Industrial practice has features which those of us engaged in institutional research can no longer ignore or overlook The necessity of a chemical engineering background for our research workers particularly those engaged in productive type of research, periodic supervision of the bench work by chemical engineers, all process study and pilot plant work exclusively in charge of chemical engineers, more stress on economy, and lastly emphasis on group or team-effort are some of the features that we may take note of with great advantage. The technological scene is changing very fast. What is discovered today becomes obsolete tomorrow. Merely opening a few new national or regional laboratories will not

help our industries unless we import new calibre into our industrial research. Our position in the world patents is lamentable. Let us no more experiment with research but profit by the mistakes which others made and paid heavily for.

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CHOICE OF RAW MATERIALS

by

DR. M. G. KRISHNA

(Central Laboratories, Hyderabad-Deccan)

Transformation of one material into another which is distinctly separate from the original and which has greater utility is the essence of chemical manufacture The primary requisites of such manufacture that have to be taken into consideration before establishing the chemical plant are —

1. The process of manufacture.
2. Availability of raw materials.
3. Availability of utilities like water, etc
4. Fuel and electricity.
5. Labour.
6. Markets for finished goods.
7 Transport facilities to and from the site to plant location.

There are other considerations, geographical, e g., but the most important are mentioned. Each of these factors is vitally important for the establishment of any chemical industry in any country. The success or failure of an industry will depend on every one of the factors and each has to be considered in relation to the other and not in isolation, if we wish to make the project a success Ultimately, we have to choose such conditions as will give us the desired product at the cheapest price.

For today's paper, I have chosen, quite deliberately, one of these factors, namely 'choice of raw materials', to provoke discussion and crystallise the issues involved I would like to make it clear at this stage, that I am not going to discuss 'utilisation of raw materials' in general, which is a much wider field. I have consciously restricted my subject to merely choice between alternative raw materials available either indigenously or from other countries, so that maximum

discussion within the available time can take place, as I believe it will I wish to examine the issues in relation to our country's present conditions, now that we have to make a beginning in its industrial development.

There are different aspects of "Raw Materials" that have to be considered before any industry is started ; they are —

1 The distance of the source of raw material from the site of industry
2 Purity
3. Alternative sources of the same raw material.
4 Alternative raw materials
5. Cost of raw material

Before we choose one starting material for any industry, we have to find out which is nearest, cheapest and purest under the existing circumstances at any time. Leaving all the other four aspects I will straightaway proceed to the main subject, the choice of raw materials ; but I propose to discuss it in relation to the other four.

There are very few industries which have only one raw material to depend upon Usually it happens that more than one type of raw material is available and we have to choose between them to make the cheapest product. Now when we think of choosing, we will come up against the standpoint from which we choose. In other words, what are the criteria of choosing between alternative raw materials ? From what angle or angles do we view a particular choice as favourable ? And, are they justified in view of our country's present requirements and economic condition ? Let us discuss these aspects Now what are the factors that govern our choice :

First : What are the various raw materials available ?
Second : What are the existing uses of the raw materials as such ?

Third : Are they essential commodities in themselves ? *i.e.*, if they are materials for food or clothing of our country's millions, should we then use them for production of materials which are not commonly required and not essential ?

Fourth : Is there any priority, not only for production of commodities but also for choice of a raw material from a number of them ?

Fifth : Are all the alternate raw materials indigenous or should some of them be imported from abroad at greater cost than justifiable ? What priority should be given to our raw materials with protection, so as to develop our country's industry ?

Sixth : Does the manufacturing process and its costs justify the selection of the material ?

Seventh . Are there any useful by-products from a particular raw material which might give preference to it over others ?

Eighth : What are the comparative costs of production of a material from different raw materials ?

Ninth : What is the purity or grade of the raw material ?

I admit these may not be all but I would not be far wrong when I say that I have covered some of the most important considerations.

I would now like to take specific examples and discuss the relative value of a raw material for a desired product from our country's viewpoint. Of course, I would like to remind you before I do so that text books on Industrial and Pure chemistry are full of examples and I am not going to inflict upon you the punishment of quoting all of them ; I will take only a few.

Let me take inorganic raw materials first.

Most of the inorganic chemicals have usually more than one raw material or more than one process of making a substance. If we have two varieties of an ore, a low grade one and a high grade one, we naturally choose the high grade ore. But supposing the high grade ore is to be obtained either from far off distances in our own country or from abroad, then we may be well-advised to concentrate the low grade ore by flotation methods and use it successfully in a given process and develop our local industry rather than import from far off distances.

Next, taking a classic example, even though of merely historical importance and interest now, the manufacture of soda by Le-Blanc process and Solvay Ammonia process using different raw materials provides evidence that development of a new process and a cheap process displaces a set of raw materials in preference to others.

Take sulfuric acid manufacture. The raw materials that are theoretically possible are : elemental sulfur, sulfides like iron pyrites, by-product sulfur dioxide from zinc and copper ores, gypsum and hydrogen sulfide I will quote the example from America

In 1880 sulfur was used exclusively. Due to relative costs the use of pyrites grew, till in 1914 only 2 5 per cent. of the acid was made from sulfur. But due to the war in 1914 and restricted imports from outside of pyrites, and better methods of sulfur mining in America, sulfur regained its place In 1940, 66 per cent. of the acid was from sulfur while 22 per cent. was from pyrites and 11 per cent was from waste gases obtained from zinc and copper ores.

Similarly in Germany, where sulfur was not available, most of the acid was from pyrites and zinc blendes and when pyrites import was restricted, they started from gypsum.

In our country where sulfur is not available and gypsum is more in stock and pyrites is also limited, we have to rely on gypsum and pyrites. Let me quote from "The Wealth of India"(1). It says, "India has no significant deposits of sulfur or pyrites . The small deposits of pyrites in Bihar and near Simla occur in comparatively inaccessible places. Since the development of the gypsum process for the manufacture of sulfuric acid from anhydrite ($CaSO_4$) in Germany and the U.K., the large Indian occurrences of gypsum in the Punjab, Jodhpur, Bikaner and Trichinopoly are likely to form the raw material for the production of the acid in India in the future. The chief difficulty will be the transport of raw material over long distances to centres of acid production. But this may be overcome by producing sulfur from gypsum and transporting it . ...Among the other possible sources of sulfur dioxide may be mentioned the waste gases from the copper smelters of Maubhander in Bihar. . .These gases have not been made use of even during the last war when there was acute shortage of sulfur . , , " Therefore our choice should be made in relation to our conditions.

You know that the Sindri Factory is raising a controversy in Parliament as well as outside it, about the distance from which gypsum is to be obtained. India has to obtain gypsum for the factory from Khewra mines in West Pakistan. The feasibility of the transport of the required raw material is being questioned

Similarly there are other examples. Now let me pass on to Organic materials where we have more examples We can classify these into :

1. Agricultural raw materials which we have in plenty.
2 Coal, in which we are not too rich.
3 Petroleum, of which we have none

Taking the first *Agricultural Raw Materials.* I will take *Alcohol.* The sources are molasses, starchy materials, cellulose-bearing materials, ethylene, etc.

We have plenty of molasses and cellulose-bearing materials and starchy products but no ethylene and hence the latter is to be ruled out here, though in Germany and the U S A. it has gained ground. But, under the present acute food shortage, starchy materials cannot also be spared. Again quoting from "The Wealth of India"(2) · "Potatoes were extensively used for the manufacture of alcohol in Germany before the War ('39-'45) During the War, owing to shortage of molasses in the U S A , immense quantities of alcohol were produced from wheat and wheat products . . . Owing to the present acute shortage of food-stuffs in India, grain cannot be diverted to the manufacture of Industrial alcohol, and only small quantities may be allotted for the production of beer and potable spirit"

Hence, we have to develop our alcohol production more on molasses and cellulose-bearing materials ; but the latter process is much more costly, leaving molasses as our best choice.

Taking another example, that of *Acetone* In our country the raw materials are · pyroligneous liquors from wood distillation, fermentation of starchy materials by acetobutylicum , in America oxidation of isopropyl alcohol is used as well. We have plenty of the first, *i.e.*, wood. But we cannot afford to waste our starchy foods for a solvent for explosives. But an interesting example of how the by-product usage has a bearing on one or the other raw material is shown by acetone manufacture. In America, synthesis of acetone from propylene.

derived from petroleum products resulted in lesser production of acetone by the fermentation method But when later on they found that normal butyl alcohol, which forms 60 per cent. of starch fermentation products, is useful in rubber manufacture, fermentation process again gained ground.

Again, take *oxalic acid* as example The use of this product is limited to the printing and dyeing of textiles Its sources of preparation can be saw dust, sugar, sodium formate from sodium hydroxide and carbon dioxide. Of these we have to choose the raw material most sensibly. For example, I think we cannot afford to oxidise sugar simply because sugar is cheap and pure and can be made available in large quantities. This can be done only by poeple who do not think in terms of *national welfare* and by those who wish to make money on the high price of oxalic acid.

Next, we have our *vegetable oil seeds* In these days of fat deficiency in the diet of our population we cannot afford to use those oils which are mostly used for *edible purposes* for non-edible purposes like soaps, drying oils, etc. We have to use only non-edible oils and those edible oils which are used in lesser quantities. And this aspect was sufficiently brought out during the last two days Similarly our coal resources which are not too good nor too much, have to be dealt with carefully. We have to see that we do not waste our material and that we use it properly

Therefore, all the examples given so far clearly show that when we have to choose a raw material we should do so only after duly considering the existing uses of the material, the relative importance of the uses of the product and not merely the price that the product would fetch in the market

The one important question now is, what is the research we have to do in our country under the existing conditions ? It is obvious that while we should not only choose the correct raw material but also see that, if we do not have any alternative, we must devise processes wherein we can choose our existing raw material. Therefore, I plead that if we want to develop our country's resources fully and increase our prosperity, we must have a highly planned and fully co-ordinated method of choice of raw material, giving at every stage priorities to the utilisation of raw material not for fancy, or for earning profits, but for

production of more essential commodities. We must plan our research in the industrial laboratories to work out most economically our own raw material, so that our industrial production may not be killed by foreign competition. Also, I would go so far as to say that we have to plan the industrial development in such a way that we do not use the essential commodities for producing either less essential or luxury goods simply because the latter fetch more money to the producer. Such tendencies on the part of the industrialists, in my opinion, must be curbed and treated as anti-social

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(1) "The Wealth of India," Industrial Products, Part I (1948), p. 19

(2) Ibid., p. 53 & 54.

(*Monday*, 14*th August* 1950).

DISCUSSION.

Those who participated were :—

Mr. Abde Ali, Department of Applied Chemistry, Osmania University, Hyderabad-Deccan.

Dr. M. R. Mandlekar, Department of Industries, Bombay.

Dr. S. H. Zaheer, Central Laboratories, Hyderabad-Deccan.

Dr. M. S. Iyengar, Central Laboratories, Hyderabad-Deccan

Mr. Baldev Singh, Central Laboratories Hyderabad-Deccan

Mr. A. Rahman, Central Laboratories, Hyderabad-Deccan.

Participants in the discussion agreed on the necessity of looking into the *suitability* and other considerations *regarding the choice of raw materials* and the *importance of pilot plants* in giving useful data regarding costs and other important technical factors It was, however, pointed out (S.H.Z.) that the speaker had not mentioned *sulphur from the Thylox process* as an important source for sulphuric acid. Similarly the speaker had omitted the mention of *alcohol as a material for acetone.* Alcohol was of great significance for Hyderabad state since the Sirsilk Industries have used the cellulose acetate process in preference to the viscose process in their rayon factory. Replying to the discussion the speaker

(M.G.K.) admitted that he had naturally not mentioned many other sources as examples since his idea was only to illustrate his point with an example.

The utilization of waste products had not been mentioned by the speaker ; it was pointed out (M S.I.) that in the choice of raw material it is rather important that the utilization of the waste product should be looked into , *e g.*, groundnut husk can be used to make activated charcoal as shown by experiments now being carried out in the Central Laboratories, Hyderabad-Deccan. Refuting the point made by the speaker *regarding low coal reserves and their inferior quality*, it was stated (M.S.I.) that it was incorrect to describe India's coal reserves as low and with regard to their quality it is necessary to look at the whole problem freed from conventional ideas. Much depends upon the particular use one has in view when determining the quality of coal Hyderabad coal can yield coke which is used as a reductant in electric furnaces for metallurgical purposes in Sweden Regarding waste products, the speaker (M.G.K.) said that he realised their importance ; a waste-product could become a useful by-product once its uses were established. Regarding coal, he said he had taken the traditional view as we have yet to know our resources fully and find uses for the type of coal we possess.

Attention was also focussed (B S) on *substitute raw materials* for developing industry with regard to national and regional needs and demands, for example, the developing of plastic fibers in America as a substitute for jute, or of the synthetic dye industry in Germany to reduce dependence on foreign imports. It was also pointed out (B S.) that the speaker (M.G.K.) had not mentioned a very important raw material of India, namely indigenous drugs It was stressed that the products of our indigenous plants were quite comparable to imported products. It is essential that the forest resources of our country should be developed in order to manufacture, for example, Nux Vomica, belladonna, podophyllum and other drugs

There was considerable controversy over the *relative use of a raw material* for nutritional purposes and industrial utilisation The speaker (M.G.K.) had mentioned that raw materials like sugar should not be used for production of less essential chemicals like oxalic acid, because of the scarcity and nutritional uses of the raw material On the contrary, it was stated (S.H Z.) that sugar was one of the most widely

available of organic materials, obtainable moreover in a pure condition, and there is no reason why it should not be used ; regarding its scarcity, this is only temporary and due to monopolistic conditions The other point of view stressed (M.R.M.) was that potatoes and bananas are more important nutritionally than for the manufacture of starch or glucose, especially when they are not available in sufficient quantities for the needs of the people Under the Bombay Government's scheme in the "Grow More Food" campaign, good crops of potatoes and sweet-potatoes were obtained and soon the industrialists were rushing to obtain permits to manufacture starch in their factories ; it was clearly not desirable to encourage them in this Replying to the controversy regarding the relative priority of any material for nutritional or industrial use the speaker (M G.K) maintained that nutrition has to be given first preference though he conceded the point that one need not be very rigid and that some concession has to be given in the case of the manufacture of some important materials, like calcium gluconate

Regarding *the attitude of industrialists and the condition of industries* it was pointed out (S A S) that Indian industrialists are guided by extremely short-sighted policies ; interest in Industry and its development does not seem to be their attitude. Many industries exist merely in name ; for example the pharmaceutical industry of India was merely a bottling industry Many industries who employ chemists do not give them research facilities and time for research Some of the industries are started on wrong premises like the Sindri Fertilizer Project, where the choice of ammonium sulphate itself was, in his opinion, a wrong choice as India does not possess any gypsum resources. In this connection it was pointed out (A.A) that gypsum was available as a by-product of the salt works in Travancore It was agreed (S.A S.) that selection and availability of raw material should not be the main criterion in deciding in advance the growth of industries. England, for example, is importing most of her raw materials but still has a flourishing Industry The economics of the finished products also count Viewed from this angle there is no reason why a cheap raw material like sugar should not be used for making chemicals otherwise imported from other countries.

The *industries in India are not developing properly* ; there is lack of capital, lack of proper organisation and more than one other adverse factor. Capitalists are not intrinsically interested in industries, their interest

lies only in the returns. In view of the above factors and the fact that technicians are responsible for the success of any industry, it was suggested (M.R.M, S.A.S.) *that technicians should combine in a sort of a co-operative to run the industries* and ask Government for help. This alone can help in the proper development of industries in India. In a criticism of the above proposal, it was suggested (A.R.) that an analysis of the whole problem of why the industries are not developing in India was necessary. Such an analysis will help us to remove the factors impeding growth The idea of cooperatives, it was stressed, though good, is out-dated ; it belongs to the 16th century growth of science, when people like Agricola preached and practised science The growth of society has increased the complexity of the problem and especially the financial requirements of industrial research, and state planning is the only solution. There is a lot in the example of the U S S R where State planning led to a great and rapid industrial development of the country The value of large scale planning is being realised in the U.K and U.S A. also

President's concluding remarks.

The President (B S K) in conclusion remarked that we have to give serious thought to the points raised during the discussion. In discussions like the one above social, political and other factors also creep in and we have to be careful in taking notice of them and not emphasise them unduly at the cost of technical factors He stressed the importance of the suggestion made by Dr M. R Mandlekar regarding the organisation of cooperatives by scientists to enable the industries in India to develop

OPERATIONAL RESEARCH AND THE TIME-LAG BETWEEN RESEARCH & INDUSTRIAL APPLICATION

by

A. RAHMAN

(Central Laboratories, Hyderabad-Deccan)

The present paper suggests a possible use of Operational Research. It does not aim at solving the problem of the time-lag between research and industry, which is colossal, but limits itself to suggesting a method which, if utilised, can go a long way towards reducing the time-lag. The problem of time-lag is the problem of the industrial, social and technical relations of science. The paper briefly gives an analysis of factors responsible for the time-lag between an invention and its industrial utilisation, and suggests a scheme to eliminate the latter at the laboratory level.

In the first place we would like to restate the problem in the form of the following questions .—

1. Is there a time-lag between an invention and its industrial utilisation ? If there is, then
2. Is it important enough to be removed ? If so, then again
3. How far can it be reduced and how ?

Considering the first question we take the liberty of quoting from the article of S. G. Gilfillan, published in the U.S. Government's report on Technological Trends :

" Taking nineteen inventions voted most useful, introduced in 1888-1913, the average intervals were : Between when the invention was first merely thought of, and the first working model or patent, 176 years ; thence to first practical use, 24 years ; to commercial success, 14 years ; to important use, 12 years ; or say fifty years from the first serious work on the invention. Again, in the study of most important inventions of the last generation before 1930, in Recent Social Trends, a median lapse was found of 33 years, between the " conception date " corresponding to the second above, and the date of commercial success.

Searching for exceptions, it is hardly possible to find an invention which became important in less than ten years from the time it or some fully equivalent substitute was worked on, and few did in less than ten years from the time it or some fully equivalent substitute was worked on, and few did in less than twenty. Here is, then, an excellent rule of prediction for the present study -to predict only inventions already born, whose physical possibility has therefore been demonstrated, but which are usually not yet practical, and whose future significance is not commonly appreciated." [vide Social Functions of Science, J. D. Bernal, P. 161, (1939)].

This quotation not only points out that there is a definite time gap between the 'conception' of an invention and its industrial utilization, but it also suggests the different stages of any invention. From the viewpoint of our analysis, we find —

1. There is usually a big time-lapse in the application of a theoretical discovery It may take a long time for the social and industrial implications of a discovery to be appreciated.

2. Once the applied side is understood, or its implications realised, its utilization is hastened, and though the time-lag is reduced it still remains considerable

3. From the historical point of view the time-lag in the first and also in the second stage of industrial utilisation of a discovery is considerably reduced after the first decade of the twentieth century compared to the previous decades. An enquiry into the cause of the above being so will also reveal the factors that have reduced the time-lag. We will take this up later.

Before we take up the analysis of the points emerging from the above quotation we ought to question whether it is really necessary to reduce the time-lag. In our opinion it is necessary in order to develop our industries. Time-lag means lagging behind technically, socially and scientifically. Further, whereas the idea in the older industries was merely that of *continuity*, *i.e.* to prolong and maintain the existing condition of an industry, the idea that has come to dominate, through historical reasons, modern industry is one of *progress*, *i.e.* of change from the existing conditions to a newer and a higher level. This means,

in other words, the utilisation of newer and yet newer theoretical discoveries in industry. That is why this subject of the time-lag is important and needs our utmost attention and resources.

Let us first take the point suggested by Gilfillan, which can roughly be called a gap between theory and practice.

The lack of appreciation, or appreciation, of a particular invention is dependent upon the nature of the discovery, social conditions and social requirements, technical development and communications of a particular period. And one must realise here that not only are these inter-dependent upon each other, but put together they all form the pattern of a period which is considered in this field as of a historical and evolutionary order.

We will here take four examples to illustrate the impact of the factors mentioned above :—

I. Nature of discovery.

This may be intellectually in advance of the period ; for example, in the field of mathematics —

" Hero had announced that the area of triangle of sides a, b, c, was $\frac{1}{4}\sqrt{(a+b+c)(-a+b+c)(a-b+c)(a+b-c)}$, a form of statement which the early Greeks would have found meaningless, since it needed a four dimensional space for its geometrical representation But this form of statement was so unusual that Hero apologised for multiplying four factors, where only three could be represented in a diagram" [vide J. Jeans, Growth of Physical Science, P 85 (1947)] We have of course taken a very abstract case to illustrate our point more fully.

II. Advanced technical nature.

(a) " The first Dunlop Pneumatic tyre appeared in 1888 ; but the idea was not wholly new Like many other things before and since, it had been invented before its time, that is to say before manufacturing was sufficiently advanced to make it practical." [Henry Tizard, Presidential address delivered to British Association (1948)].

(b) Another more illustrative case is the attempt of Charles Babbage in the 19th century to build a calculating machine.

III. Social conditions and requirements.

How these affect our case is well illustrated by the following examples .—

(a) Gun powder and printing, as against the above mentioned example, spread almost immediately after their discovery, solely due to social requirements.

(b) Growth of the ethylene industry, solely due to German national reasons

(c) Mendel's work was buried for lack of proper communications and the necessary social impetus, while in our times the need for food has resulted in the intensification of genetical research and in the application of research techniques to problems of agriculture.

IV. " Social Interests " affecting utilisation.

This takes us back to the second point that emerged from the quotation from Gilfillan, *viz*, to the causes for the continuation of the time-lag, despite proper appreciation and realisation of the utility of a discovery in industry.

In the lecture delivered yesterday, Dr. S. Z. Ali spoke (see this symposium, page 74)) on the utilisation of X-ray in coal analyses. X-rays were discovered by Rontgen in 1895 and its first utilisation for the analyses of materials was demonstrated in 1912 by von Laue. Yet even today we find that X-rays are not being used outside laboratories Why is it that the immense possibilities regarding methods of analyses once shown are not being utilised ?

To answer this question let us consider the following —

(1) Lack of well-equipped research laboratories, with sufficient finances for the necessary apparatus. This has been considerably neutralised by the recent interest of various national governments in industrial research, even though their effort is mainly devoted to purposes of war.

(2) Vested interests of the industrialists. This is specially so with our rather anarchic system of society where the interest of an individual comes before the interest of society. A particular person who has invested a large sum of money in the industrial utilisation of a process, would prefer to continue his process, even though it becomes out-

of-date, just to safeguard his profits, rather than scrap the old method of production and start producing by new methods, about which he feels vague and unsure. Such an approach leads to technical and scientific backwardness. This occurred for example during the 19th century in England, which lost its leadership in optical and chemical industries to Germany, resulting in the actual transfer of industries from England to Germany This is again evident at the present time in England This time America has snatched the leadership from Britain for precisely the same reasons [for details, see the Report on the State of British Industry].

Another aspect of these vested interests is the resultant misuse of patents Patents are not only merely suppressed and bought, but potential discoveries are abandoned to safeguard the vested interests of industry and the competition between various companies (for details please refer to the "Evidence of the Federal Commission on Communication," U S A., and Dr Levinstein's "British Patent Laws, Ancient and Modern")

To sum up the above analysis, what we wish to stress and want you to realise is that the translation of a laboratory discovery to the field of industry is not merely one of scale and intensity The transfer is not effected smoothly and, consequently, there are gaps at various stages which are a retardation of progress Further, new forces of social origin and nature enter into play, and have a far greater effect than purely technological and scientific problems In consequence, they should not only be kept in mind, but carefully analysed and conclusions drawn from them, as this is essential for technical development

Let us now go back to the third point that emerged from the analysis of Gilfillan's data, *viz.*, that the time-lag is much less in decades after 1910 than in previous decades. One is naturally led to enquire, what are the new factors that have emerged in our times that were not present in previous decades ? Surely these would throw considerable light on our problem. Of course we should endeavour to be cautious in our evaluation since there may be, and probably are, many discoveries that are lying unexploited in our times which when exploited sometime in the future, will cause our own period to be called a period of lag. Nevertheless we do find a considerable hastening up of industrial exploitation of discoveries in our period, especially since the beginning of the Great War. Briefly these new factors are :

(1) Increase in the number of scientists.

(2) Greater research facilities (laboratories, funds, etc.).

(3) Growth of scientific organisations, greater communication of scientific literature, etc

(4) Growth of industry.

(5) Closer co-operation between scientists and industrialists.

The fifth point, *viz*, the closer co-operation between scientists and industrialists, is much emphasised these days. According to Sir Edward Appleton "We believe that many of the problems which face industry cannot be satisfactorily answered from a card index or often by the written word For effective collaboration, the scientist and the industrialist must somehow or other be brought into personal contact" [vide Research in Industry, H M S O, P 5 (1948)]

Should we draw the conclusion from this that a quantitative increase of these factors will accelerate the process of bringing industry and science together and will decrease the time-lag ? We feel that this is not so, as there is no direct and linear relationship between the above factors and the the time-lag It is a quantitative as well as a qualitative problem The above factors can influence the time-lag only to a certain extent as they rule out newer forces that have come into play, as pointed out before, and the neglect of the qualitative nature of the new feature is not a proper approach to the problem They aim only at a patch-up of new features as and when they appear

What then has this new approach to be ? This question brings us to our point of what method we should follow in reducing the time-lag According to us Operational Research is the only tool. But before we suggest the method we must clearly keep this in mind, that the subject has to grow, and like any new potential industrial process, has not been standardised ; this may be considered as a confession, as it were, of an Operational Research worker

There is controversy amongst those who are acquainted with the method of Operational Research in regard to its applicability to the peace-time problems of construction [vide Sir Henry Dale, Nature, **160,** 660 (1947) ; J G Crowther, "Science at War," article on "Operational Research," H.M.S.O., London (1947)]. Many who think it can be applied to peace-time problems of science and industry

limit it to what was previously known as " market research " in America (Charles Kittel, Science, 105 (1947), February 7), or consider it to be at most a quantitative method helpful in taking executive decisions [Sir Charles Good-Eve, Nature, **161,** 377 (1948)].

If we limit ourselves to the above definitions, we will not be able to realise its newness and, further, our understanding of Operational Research will also not enable us to fully appreciate the role it can play in extending the domain of science to fields not covered so far by orthodox scientific methods. Lack of appreciation of such a role is, unfortunately, due to military secrecy which still keeps the data obtained during the military operations of World War II a closed book. The vagueness that still surrounds Operational Research is primarily due to this circumstance, while the other factors that have hampered its recognition are its newness and its ambit of work.

Operational Research utilises methods used in classical science and in the developing field of statistics in such a manner as to be the basis of a new branch of science. Its field is peripheral to the field of classical science and actually lies between the field of what is commonly known as " Pure Science " and " Applied Science," and also covers the field of industry. The field of industry in the early period of the growth of science was actually regarded as the province of science and scientists, as is evident from the works of Agricola and the proceedings of the Royal Society of London at the time of its inception, but later on it became solely the domain of industrialists who had nothing to do with science and were not scientists. Industrialists who owned the completed technical processes and exploited them, considered industrial problems outside the scope of science and resented the scientist's approach, like the army General in World II who did not like the invasion of the " slide rule " into methods of warfare, objecting, of course, to the intrusion of an operational research workers' team.

This division between science and scientists on the one side and industry and industrialists on the other is important. It is one of the main causes of the time-lag. Bringing the two units together cannot be achieved by the method suggested by Appleton, since what is needed is to effect a transfer. We have to consider such isolated stages in a vast phenomenon in relation to the whole and this Operational Research sets out to do.

There is a tendency to take for granted a problem. An Operational Research worker starts from the very beginning. Is it a problem ? Is it a problem worth taking up ? Is it a short-term problem or does it need time for solution ? Can the laboratory take it up ? Does it fit into the programme of the laboratory ? What is the nature of a problem ? Is it technical, organisational, etc. ? These questions and many more are supposedly commonsense questions, but their being so need not lead us to minimise their importance. We must bear in mind that the choice of a problem determines a series of other questions that ultimately arise at a later stage as the problem progresses towards a solution Operational Research gives a quantitative basis to such decisions

It will be quite in place to raise here the question why is it that, in spite of the energies being devoted by so many eminent scientists to administration and organisation, scientific research carried out in our laboratories in India is not being utilised for industrial development ? In a very large number of cases we are forced to realise that it has been so simply because we did not ask the commonsense questions mentioned above before taking up the problem. These queries are essentially a stage of research which can roughly be called the stage of " Library Research." It will determine the growth of the problem in the same manner as the pilot plant determines the industrial development of the process. It not only gives a quantitative basis to what is to come, *i.e.*, to the prediction of results, but also bridges the gulf between the laboratory and industry which, as we have seen, is the main cause of the time-lag. Let us not forget the old saying : " Forewarned is forearmed."

In an industrial laboratory the research that is carried out is primarily threefold in character. It is either directed towards making a product which is intended to fill in a gap in the normal supplies of any material ; or it aims at a substitute for an already existing material ; or lastly it may aim at creating an entirely new source material. Any research that is envisaged for either or all of these three aims is socio-scientific in nature. But when it is being tackled by a research worker, all he bothers about and rightly so is the pure or technical aspect of his research, and he very much resents any intrusion or diversion. To him the socio-scientific aspect comes into play, if at all it does, only when he has completed his problem. But at this stage, before the specialist carries out the laboratory research, he may be made part of

a unit, other members of which, without bothering the research worker, carry out what has been termed library research ; they go into questions regarding the raw materials, their availability, costs, etc., the economics of the products already in the market, and the economics of their product when that is ready for the market. A chemical engineer is put on the job of designing a pilot plant bearing in mind the technical solution and the economic side of the problem. In this way many changes which are usually referred back from the industry can be anticipated at the pilot plant stage and adjusted.

Before the solution is put on a pilot plant level it is desirable that an internal report be circulated in the laboratory. This may yield rich fruit since quite often a worker in a different field may suggest a simpler and more economical step in the process.

At the pilot plant stage many factors have to be taken into account which may ultimately determine the success or failure of the process. These roughly fall under the following heads :—

i. Preliminary estimate of full scale production costs.
ii. Quality of the product.
iii. Efficiency of the process.
iv. Materials of construction, instruments, technicians, their availabilities and costs, etc.
v. Distribution and marketing of the new product.

After the pilot plant stage, when the process is passed over to industry, the process has to be followed closely. The methods of observation are mostly known and are followed in highly industrialised countries to varying degrees and are now accepted as within the field of operational research. These will be enumerated here, in order to clarify the comments that are made later.

i. The training of technicians who will run the processes, the problem of monotony of work, conditions of work, fatigue of human labour leading to inefficiency, etc. These should be gone into with particular reference to the conditions in different areas.

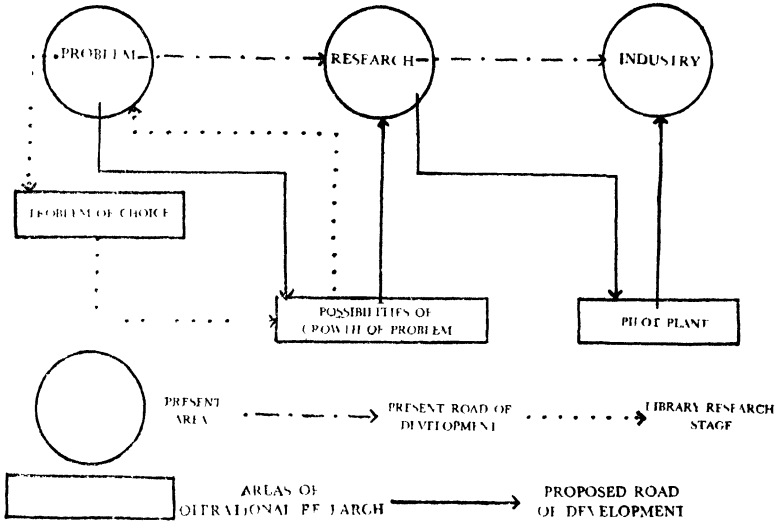
ii. Process control, analysis and testing, calibrating and checking of instruments and collection of chemical data with a view to evaluating efficiency.

iii. Plant performance and efficiency.

iv. Statistical data.

All this involves more persons than a chemist alone and should be the work of a team comprising a chemist, chemical engineer, statistician and planner. This work can be taken up by such a team when the industry is working, but actually it is not something which starts at this stage but is, as a matter of fact, a continuation of the work of earlier stages. And a unit consisting of the necessary personnel when formed at the very beginning of the work, will have a greater grasp over the problem and consequently will be able to advance more suitable solutions.

Only such a team can bridge the gulf between scientist and administrator, reduce the gaps at various stages and finally put the problem of production on a scientific footing. What all this means in theory and practice is to correlate one stage of research with the other, and make the whole an organic and complete entity.



It must be stated in conclusion that we should keep in mind the following points when considering the above scheme :—

1. We must guard against rigidity.

2. The scheme of proposals has omitted social factors which should strictly form part of any programme of overall scientific development.

(*Wednesday 16th August*, 1950)

DISCUSSION

Those who participated in the discussion were :—

Dr. M. R. Mandlekar, Department of Industries, Bombay.

Dr. S. H. Zaheer, Central Laboratories, Hyderabad-Deccan.

Dr. G. S. Sidhu, Central Laboratories, Hyderabad-Deccan.

Dr. K. T. Achaya, Central Laboratories, Hyderabad-Deccan

Dr. M. G. Krishna, Central Laboratories, Hyderabad-Deccan

Dr. N. Shanmukha Rao, Central Laboratories, Hyderabad-Deccan.

Dr M S. Iyengar, Central Laboratories, Hyderabad-Deccan

Mr L M Srivastava, Central Laboratories, Hyderabad-Deccan

Mr G. Satyanarayan Rao, Central Laboratories, Hyderabad-Deccan.

Mr. Baldev Singh, Central Laboratories, Hyderabad-Deccan

Mr Bharat Bhushan, Central Laboratories, Hyderabad-Deccan

' *Will the institution of Operational Research completely remove the time-lag* (G S R.) ' " In answer to the above question it was pointed out (A.R.) that Operational Research aims at investigating the factors that are responsible for the lag and that are to be eliminated. All the causes cannot be eliminated completely as they are of different origin and are the results of modern life A certain lag may be inevitable in some cases

With regard to the *factors causing time-lag*, it was said that some, like demand for a product, *may be quite outside the scope of Operational Research* (L M.S.). It was pointed out (A.R.) that as a generalisation methods of operational research can help to reduce the time-lag.

To elucidate the point raised (G.S S.) regarding the *usefulness of Operational Research in fundamental or University research*, it was stated (A.R.) that the main field of operational research was the industrial relations of science. Its use in a University is mainly academic, since at this stage students should be given an insight into its methods.

It was suggested (K.T.A.) that nationally there may be *differences in the stage at which the time-lag occurs*, for example, in India the time-lag between conception and patent was far less than that between patent and practical use, though in the data given for western countries the case is just the opposite. This may be true, but it has to be investigated and there is great dearth of data on Indian conditions (A.R.).

Though it may be quite true that industry should take advantage of research it must be borne in mind that the *pace of research is faster*, and industry has to be conservative if it is to develop economically, though on occasions this development can be speeded up, as in the case of the atom bomb, to accelerate industrial progress (L.M.S.) The latter, it was said (B.S.) was due to vested interests and these can help to reduce or to increase the lag. In this respect the example of the U.S.A. and U.S.S.R. should be borne in mind. In the former patents lead to an increase in the gap, while in latter, constructive interests have reduced it.

Social factors that affect the growth and development of industries and the time-lag, were the basis of considerable discussion (S.H.Z., L.M.S., M.S.I.) It was said (M.G.K.) that in a practical case social factors cannot be avoided. For instance, though there was maximum co-operation between technicians and industrialists during the war, and hence little time-lag, after the war things have taken a different shape. Many, like the textile industrialists, not pressed by any exigencies of war, were reluctant to change their outdated machinery. Operational Research brings such factors into focus, especially where the aims of discoverer and industrialist are divergent, which increase the time-lag and make it inevitable, as in India. If the state was the industrialist such factors may not be present and thus the time-lag will be at a minimum. Regarding the decline of the textile industry in Britain there was some disagreement. It was pointed out (B.B.) that the decline of the industry was mainly due to the economic dependence of the U.K. on the U.S. Attention was also drawn (M.G.K.) to the report published by the British Government on Coal, where the chief factor responsible for reduced production was said to be the non-replacement of outdated machinery in the mines.

It was further stated (A.R.) that *factors hindering the application of science in industry* was one matter and their removal was another. Operational Research can only indicate the impact of social factors and

point to their removal ; this had happened for example in the USSR, where the state took the lead in removing these impediments, leading to a successful development of industry. Further, Operational Research bridges the gulf between research and industry, channels a problem, and helps co-ordinate the various stages of the development of a problem and thus reduces the time-lag This is necessary today when there is a centripetal tendency in science and industry , no one individual can bridge the gulf, as was the case in the early period of industry.

If sociological factors can account for the lag, how can we explain the *differences between the two democracies* and why is it that the U.S.A. relies on newer methods unlike the U.K. (N.S R.) ? It was stated that in this case (A.R.) reliance on newer techniques was due to historical reasons Germany wrested the leadership in scientific industry from Britain by the use of systematic scientific methods Similarly in the U S.A , the severance of ties with Britain in 1776 left her with two courses, either to develop the new country by relying on new techniques or to be subservient to Britain The former course was chosen, which was understandable historically But today in the U.S.A. there is a tendency not to discard outworn techniques and to play safe as far as profits were concerned.

In conclusion it was stated (A.R.) that the aim of the paper was to explain how a scientist could help to solve the problems of his country by evaluating factors that affect any situation ; in this way he could help industry, even though in a limited way.

President's Concluding remarks :—

The President summing up said that the problem of the time-lag between research and industry and the social factors affecting both had been fully discussed He emphasised the need for machinery to co-ordinate the various stages of research, including industrial research and market research. He said that the location of this machinery was a matter of debate—whether it should be in the University, in Industry or in the State.